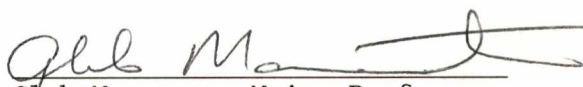


To the Graduate Council:

We are submitting herewith a thesis written by Anthony Dewayne Hipps entitled "Photochemical Investigations of Surface Adsorbed Polycyclic Aromatic Hydrocarbons, Part A: Pyrene Vapor-Adsorbed on Ferromagnetic Particles of Coal Fly Ash, Part B: Determination of the Power of a Xenon Lamp Utilizing a p-Nitroanisole/Pyridine Chemical Actinometer." We have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

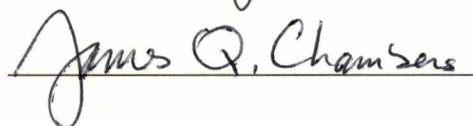


E. L. Wehry, Major Professor

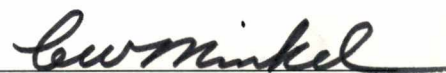


Gleb Mamantov, Major Professor

We have read this thesis
and recommend its acceptance:



Accepted for the Council:



PHOTOCHEMICAL INVESTIGATIONS OF SURFACE ADSORBED POLYCYCLIC AROMATIC
HYDROCARBONS

PART A: PYRENE VAPOR-ADSORBED ON FERROMAGNETIC PARTICLES OF COAL
FLY ASH,

PART B: DETERMINATION OF THE POWER OF A XENON LAMP UTILIZING A
p-NITROANISOLE/PYRIDINE CHEMICAL ACTINOMETER

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Anthony Dewayne Hipps

August 1989

DEDICATION

To the memory of my late grandfather, Fitzugh Lee Engle, who was such a tremendous influence on my life. He always had the time to take me fishing or talk with me. By his example, he taught me the values of hard work, honorable living, loving others, and the importance of having a good sense of humor. He is the one of the greatest men I have ever known.

This thesis is also dedicated to the memory of my late uncle, Nathan Engle. He was a wonderful uncle and good friend. He always gave encouragement and sound advice.

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Finally, this author would like to thank God for guiding and watching over him during the course of this work. With God all things are possible (Phillipians 4:13).

ABSTRACT

A magnet was utilized to collect five ferromagnetic (iron enriched) coal fly ash fractions from the bulk ashes. These ashes were then dissolved and analyzed by atomic absorption to determine their iron content.

Pyrene was deposited onto the surfaces of these ashes and two iron oxides. These samples were then illuminated with a light source similar in spectral distribution to sunlight. Adsorbed pyrene was then extracted from the substrates, and the decrease in the pyrene concentration of the substrate (ash) due to illumination was assumed to be the result of photochemical decomposition. The percentage of photodecomposition of pyrene on each substrate was calculated. The iron oxides and ferromagnetic fractions of coal fly ash showed a tendency to stabilize surface adsorbed pyrene to photodecomposition.

An aqueous chemical actinometer was developed from a mixture of p-nitroanisole and pyridine. This actinometer system was utilized to measure the power (and intensity) of polychromatic radiation from a xenon lamp (that was used to illuminate fly ash samples). Good precision ($\pm 12\%$) was observed for the power determinations utilizing this system.

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CHAPTER I

INTRODUCTION

A. Polycyclic Aromatic Hydrocarbons and Fly Ash:

An Environmental Concern

1. Fly Ash and Polycyclic Aromatic Hydrocarbons: Environmental Hazard

There is considerable environmental concern over the ubiquitous presence of two atmospheric pollutants: coal fly ash and polycyclic aromatic hydrocarbons (PAH). Both pollutants may be emitted into the atmosphere via the coal combustion process. PAH are also produced in the combustion of carbonaceous fuels (petroleum and wood) and in various industrial processes.

Coal fly ash is thought to be emitted into the atmosphere at the rate of millions of tons per year.¹ The emission of fly ash into the atmosphere is an environmental concern for two main reasons. First, fly ash contains toxic elements such as mercury, nickel, cadmium, copper, chromium, arsenic, and iron.² Second, carcinogens and mutagens are often present as adsorbates on the surfaces of fly ash particles. This thesis will focus on the latter of these concerns.

The combustion process that produces fly ash also forms PAH. The PAH are produced in the vapor phase and condense onto the fly ash before exiting the stack.^{3,4} Because there is a relationship between fly ash and PAH to mutagenic activity, the study of their physical and chemical properties is environmentally important.

Organic extracts of coal fly ash have been determined to be both carcinogenic and mutagenic.⁵⁻⁷ The carcinogenicity and mutagenicity of these extracts has been attributed in part both to the presence of PAH, and to carcinogenic analogs and derivatives of PAH, adsorbed on the surface of the fly ash.⁸ It has also been determined that PAH may react with copollutants in the atmosphere to form compounds having mutagenic properties different from those of the parent PAH.⁹ PAH may react with ozone, nitrogen oxides, sulfur dioxides and their corresponding acids, photochemical air pollutants, peroxyacetyl nitrate, and hydroxyl and hydroperoxyl radicals.¹⁰ The products of these reactions may be more or less mutagenic than the parent PAH.

Fly ash is composed of the noncombustible material present in coal. As the coal is burned the noncombustible material either remains in the combustion zone, is collected by control devices in the stack, or is expelled into the atmosphere from the stack. Depending on particle size, fly ash may remain in the atmosphere for hours or even days after exiting the stack. Smaller particles (aerodynamic diameter $<10\ \mu\text{m}$) remain in the atmosphere longer than larger particles. Much of the fly ash released into the atmosphere is in this size range because the principal particulate control technologies have low collection efficiencies for smaller particles.¹¹

This small particle fraction may present the greatest potential health hazard since small particles have the longest residence times in the atmosphere.¹¹ Because they remain in the atmosphere longer, smaller particles may have the greatest potential for human inhalation. Smaller particles are generally most efficiently deposited deep in the lungs and

least efficiently removed by mucociliary transport.¹¹ These small size fractions also tend to contain the largest concentrations (in mass of adsorbate per unit mass of adsorbent) of potential carcinogens,^{1,11} due to their larger specific surface area (i.e., surface area per unit mass of adsorbent).

2. Photochemical Reactions of PAH Adsorbed on Fly Ash

Inasmuch as PAH and their derivatives may be carcinogenic or mutagenic, the chemical reactions undergone by PAH adsorbed on fly ash in the atmosphere are a subject of considerable environmental concern. For this reason, it is important to derive some idea as to how PAH adsorbed on the surface of fly ash particles may react in the atmosphere. Of particular interest to this research are the photochemical transformations of adsorbed PAH in simulated sunlight. Do adsorbed PAH decompose in the presence of sunlight? Do PAH react to form photochemical products that may be more or less mutagenic than the parent PAH, or are they stabilized from photoreaction by the adsorbent? Inasmuch as PAH adsorbed on fly ash may pose a health problem, the answers to these questions are important. For this reason it is important to examine these photochemical transformations under real or simulated environmental conditions.^{8,10,12,13}

Chemical reactions of PAH (both in the presence and absence of light) are strongly dependent upon the physical state of the PAH. Pure solid PAH,¹⁴ as well as PAH dissolved in solution,⁷ are usually quite susceptible to photochemical oxidation when exposed to radiation in the ultraviolet region. PAH that are adsorbed on such solid substrates as alumina, silica gel,^{7,15,16} glass,⁶ soot,¹⁷ and airborne particles

obtained by high-volume filtration^{18,19} also undergo photochemical oxidation. PAH adsorbed on carbon do not undergo any detectable photolysis.²⁰

PAH adsorbed on fly ash are less photochemically reactive, in most cases, than PAH adsorbed on the previously mentioned substrates (with the exception of carbon). Some fly ash samples appear to suppress the tendency of PAH to photooxidize almost totally. On other fly ashes, PAH do photolyze, but with lower efficiency than when adsorbed on other common substrates such as silica gel, glass, and alumina.^{4,5,7,15,20-26} Identification of the physical and/or chemical properties of fly ash that inhibit the photodecomposition of adsorbed PAH is of great importance.

Those ashes that are relatively high in carbon and/or iron content are particularly effective at suppressing the photodecomposition of adsorbed PAH^{4,23,26}, as are ashes that are dark in color.^{4,7,23,25,26} It is not known how these carbon and iron fractions of fly ash stabilize adsorbed PAH to photodecomposition. One possible explanation for the ability of iron and carbon to stabilize PAH photodecomposition is the "inner filter" effect. Fly ash particles containing relatively large amounts of iron and carbon are, virtually without exception, dark in color. Because of the dark color, the incident radiation could be absorbed by the ash, rather than the adsorbed PAH. This would result in slower decomposition rates of PAH adsorbed on ashes that are dark and absorb in the same region of the spectrum as the PAH. Another possible explanation is that the carbon or iron could have some type of "chemical" influence on the photochemical stability of adsorbed PAH.

3. Iron Oxides as an Important Component of Fly Ash

Fly ash is an inhomogeneous mixture of many sizes, shapes, colors, and components.^{27,28} Virtually every chemical element can be found in fly ash. The dominant elements are silicon, aluminum, oxygen, carbon, and iron.²⁹ Significant concentrations of calcium, sodium, potassium, magnesium, and titanium have also been found in fly ash.²⁶

Iron is present in fly ash primarily in the form of iron oxides, which comprise as much as thirty percent by weight of some unfractionated fly ashes.²⁹ The amount of iron oxides present varies with the particular power plant and the type of coal being burned. Those coals that have a significant amount of pyrite (FeS_2) produce fly ash with the highest percentages of iron oxides.¹

Iron oxides are present in fly ash primarily in the form of magnetite (Fe_3O_4).^{27,29} Hematite ($\alpha\text{-Fe}_2\text{O}_3$)²⁹ and ferrite ($\text{Fe}_{2.7}\text{Al}_{0.7}\text{O}_4$)³⁰ have also been detected in fly ash. Inasmuch as they are ferromagnetic, fly ash particles containing magnetite can be separated from the bulk ash with a magnet.

Ferromagnetic fractions (particles collected from the bulk ash by a magnet) of fly ash are not pure magnetite. Elements that permeate the bulk ash may also be present in the magnetic fractions. These other elements could influence the ability of magnetic ash particles to stabilize photodecomposition. Hence, it is important to determine the amount of iron present in the ferromagnetic fractions of fly ash.

The ability of ferromagnetic fractions of fly ash to inhibit the photodecomposition of adsorbed PAH may be a health concern. Since adsorbed PAH may not decompose under environmental conditions,

ferromagnetic (magnetite) particles may retain PAH for a long period of time. Carcinogenic PAH could be extracted from these particles by the physiological fluids of the lungs after they are inhaled. Because of the refractory nature of the magnetite phase of fly ash, it has a long residence time in the pulmonary region of the respiratory tract if deposited there.³¹ This increases the probability that any adsorbed carcinogens would be extracted into the physiological fluids of the lungs.

Magnetite (Fe_3O_4) particles are by themselves a health concern. These particles, because of their crystalline silicon content, are toxicants in the lungs. Magnetite particles of fly ash may also be a health hazard because magnetite has the ability to occlude biologically active transition-metal ions such as manganese and nickel by isomorphous substitution in the magnetite spinel crystal lattice.^{30,31}

It is for these reasons that the study of ferromagnetic fractions of fly ash is environmentally important. This thesis will examine ferromagnetic fractions of fly ash in relation to their iron content and their ability to stabilize photodecomposition of adsorbed PAH.

B. Actinometry

An actinometer is a system for measuring the intensity of radiation, whether by chemical or other effects. A "chemical actinometer" is a chemical system that responds to radiation in such a way that the intensity of the radiation can be determined.

1. Relationship of Actinometry to Fly Ash Research

In this research, fly ash samples on which PAH are deposited (in

the vapor phase) are illuminated by a light source that simulates sunlight. It is important to determine the intensity of the radiation emitted by the illumination lamp for four reasons: (1) to determine the intensity of radiation (photons per second) striking the fly ash sample so that it may be possible to determine the lamp power needed to facilitate photodecomposition of surface adsorbed PAH; (2) to compare the intensity of the illumination lamp with the intensity of sunlight; (3) to make it possible to compare the intensity of the illumination apparatus used in this laboratory with those used by other groups performing similar research;^{15,21-23} and, (4) to be able to adjust the intensity of the illumination source in a controlled manner. For these reasons, a portion of this research was devoted to developing and utilizing a chemical actinometer.

2. Actinometer Systems

Various actinometer systems have been utilized for the determination of light intensity in the ultraviolet region of the spectrum. These systems include thermopile-galvanometers, various types of phototubes, and chemical actinometers.

The thermopile-galvanometer is a useful and accurate system for determining light intensity. The thermopile measures the energy of the light beam by converting absorbed light energy to heat; in turn the heat released raises the temperature of the receiver and an attached thermocouple. This creates a thermal emf relative to a similar "cold" junction which is kept in the dark. This in turn creates a deflection in the galvanometer which is then used as the measure of the incident light energy. An advantage of this system is that it is sufficiently

versatile to be useful for absolute light intensity determinations over the entire spectral range from visible to far ultraviolet.

Disadvantages of this system are that utilizing it for intensity determinations is tedious and time consuming.³²

Phototubes are electrical light-sensitive devices that may be utilized to determine light intensity of monochromatic light. There are several types of these devices: photoemissive cells, which operate as a result of the photoelectric effect or the emission of electrons from an illuminated surface; photoconductive cells, which depend upon light absorption in a solid, promoting electrons to the conduction band of the solid; and photovoltaic cells, which operate on the basis of a potential difference between cell layers on absorption of light. A major disadvantage of the phototube actinometer system is that it must be calibrated often against a thermopile-galvanometer system due to fatigue. Also, many such devices show poor sensitivity in the ultraviolet region.³³

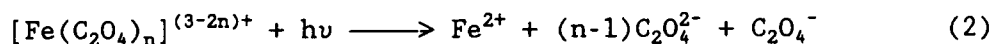
Chemical actinometers are viable alternatives to other systems for determining light intensity. These systems provide ideal secondary standards which are most useful for rapid and highly accurate light intensity determinations.³⁴ A chemical actinometer is made up of a reactant (A) which, upon the absorption of electromagnetic radiation ($h\nu$), reacts to form a photochemical product or products (B).



The quantum yield (Φ_p : ratio of the number of product molecules formed, or reactant molecules destroyed, to the total number of incident photons) must be known. The power of absorbed radiation (in photons per

unit time) can be determined from the absorbance of the reactants, the quantum yield of the reaction, the time of illumination, and the amount of photochemical product produced. Potassium ferrioxalate,³⁵ uranyl oxalate,³⁶ o-nitrobenzaldehyde in a thin film of poly(methyl methacrylate),³⁷ and a mixture of p-nitroanisole (PNA) and pyridine (PYR)³⁸ are a few of the systems that have been utilized as chemical actinometers.

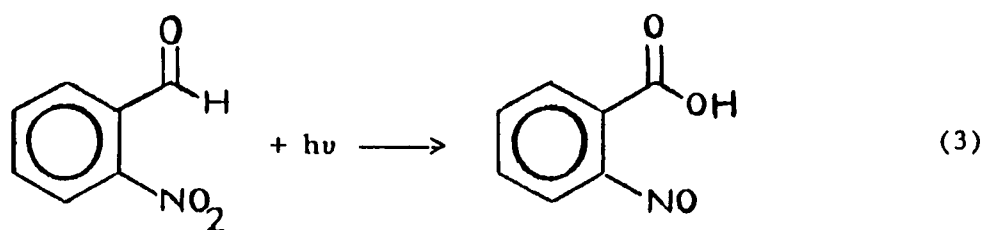
Potassium ferrioxalate is the actinometer used most extensively by photochemists. Ferrioxalate undergoes photoreduction of known quantum yields when exposed to light over a wide spectrum of wavelengths (577-250 nm):³⁵



Disadvantages of this actinometer are that it is subject to thermal decomposition at wavelengths less than 436 nm, it has a complex stoichiometry, its quantum yield is dependent on the wavelength of radiant light, it is limited to wavelengths of greater than 250 nm, and it is somewhat difficult to prepare and analyze.³⁵

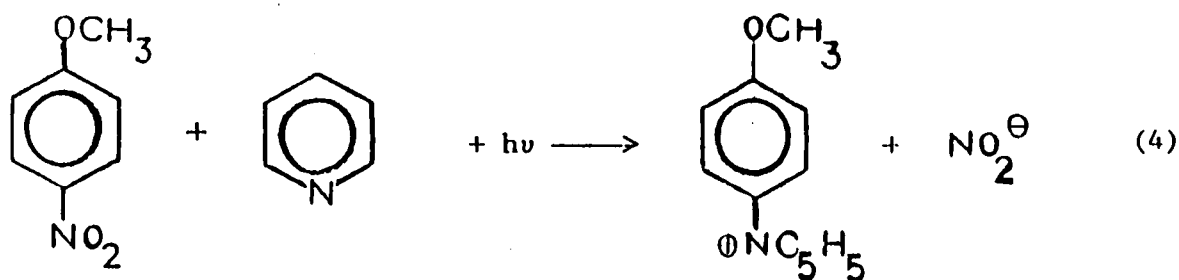
The uranyl oxalate actinometer is also used as a light measuring device. This actinometer depends on the uranyl ion-photosensitized decomposition of oxalic acid, although the reaction is of complex stoichiometry; CO, CO₂, HCO₂H, U⁴⁺, and H₂O appear to be the major products. This actinometer is prepared by mixing UO₂SO₄ and H₂C₂O₄. The reaction occurs in the range 435-208 nm, which is an advantage for intensity determinations in the ultraviolet region. The disadvantages of this system are that it has complex stoichiometry and is difficult to prepare.³⁶

A polymer film actinometer has been utilized to measure light intensities in the range 300-410 nm. This actinometer is composed of a thin film of poly(methyl methacrylate) in which the actinic material, o-nitrobenzaldehyde, is dispersed. On absorption of light o-nitrobenzaldehyde photoisomerizes to o-nitrosobenzoic acid.³⁷



Advantages of this system are that the stoichiometry of this reaction is simple and it is easily analyzed by infrared spectrophotometry. Disadvantages are that polymer films of uniform thickness are difficult to prepare and the wavelength range of this system is limited to the near ultraviolet (wavelengths > 300 nm).

The p-nitroanisole/pyridine (PNA/PYR) actinometer is an aqueous system that absorbs radiation in the range 410-220 nm. On absorption of light p-nitroanisole reacts with pyridine to form a pyridinium salt.³⁸



This system has several advantages over other actinometer systems that have been utilized to determine ultraviolet light intensity. The PNA/PYR actinometer is relatively easy to use, has simple

stoichiometry, absorbs in the ultraviolet region of the spectrum, is easy to prepare and analyze, and is relatively inexpensive compared to the other systems. It is for these reasons that the PNA/PYR chemical actinometer was utilized as opposed to the other systems for this research.

3. Power Determination Utilizing Chemical Actinometers

A chemical actinometer may be useful for light power (or intensity) determination if it meets certain criteria. The actinometer must absorb radiation at the wavelength that is being emitted and the product quantum yield (Φ_p) of the photochemical reaction must be known or determined. The quantum yield of the actinometer must be rather insensitive to changes in temperature, concentration of reactant, light intensity, and the wavelength of absorbed light. The actinometer should be sensitive enough to the radiation for a detectable photochemical reaction to occur, but not so sensitive that the reaction proceeds completely to photochemical product during the time of illumination. Also, the analysis of the photochemical product should be simple and precise.³⁴ When it meets all of these criteria, a chemical actinometer may be utilized to determine the power of electromagnetic radiation.

The actinometer is made up of a reactant or reactants which absorb radiation at the wavelength of interest. The concentration of the reactants ($[A]$) in moles per liter is adjusted to the required range. The reactant is then placed in a photolysis cell having a known path length. The actinometer is exposed to the incident radiation for a known amount of time (t , in seconds). After being exposed, the actinometer is analyzed to determine the amount (number of molecules) of

reactant that reacted (n_a) and/or the amount of photochemical product formed (n_b).³⁴

The power of the absorbed radiation is calculated from the chemical actinometer equation, Equation 7. First, the fraction of incident light absorbed by the reactants is determined. This is calculated from known values of molar absorptivity, ϵ , molar concentration of reactant, $[A]$, and path length, b , where

$$\text{Fraction of incident light absorbed} = 1 - 10^{-\epsilon[A]b}, \quad (5)$$

or determined experimentally by photometry where

$$\text{Fraction of incident light} = 1 - 10^{-\text{Absorbance}}. \quad (6)$$

After all of the variables have been determined, they are substituted into the chemical actinometer equation in order to calculate the power (P_o^i).³⁴

$$P_o^i = n_b / \{\Phi_b t (1 - 10^{-\text{Absorbance}})\} \quad (7)$$

The power is determined in photons per second. Intensity is determined by dividing power by the surface area of sample exposed to radiation.

The goal of this actinometry research was not to determine the exact power of the illumination lamp; rather, it was to obtain a close estimate of the lamp power over the wavelength range of light emission. The precise power of the illumination lamp is difficult to determine because the emitted radiation is not monochromatic and the absorbance of the reactants varies with wavelength. Prior to this research, actinometers had almost always been utilized to determine the power of monochromatic light, one exception being the studies of Dulin and Mill with chemical actinometers to determine the intensity of sunlight.³⁸

It is possible to determine accurately the absolute power of monochromatic radiation utilizing a chemical actinometer. When utilizing a chemical actinometer to determine the power of monochromatic light, it is assumed that the absorbance of the reactants (substituted into the actinometer equation, Equation 7) and the power output of the radiation source are constant at the wavelength of illumination. These assumptions do not hold true when illuminating with polychromatic light. One reason for this is that absorbance of the reactants over a wavelength range is not constant, but varies with wavelength (absorbance is a function of wavelength). A second reason is that the power output of the illumination source also varies with wavelength. Thus, the best that can be done when utilizing a polychromatic light source is to achieve an estimate of the average radiant power over the wavelength range. This is accomplished by determining the average absorption of the actinometer over the wavelength range and substituting this value for absorbance in Equation 7 (p. 12). Determination of the average absorbance is discussed in detail in Chapter 2.

C. Research Plan and Outline of Thesis

1. Fly Ash Research

The first objective of this research is to determine the extent to which fly ash fractions that are high in iron content stabilize adsorbed PAH from photodecomposition. This phenomenon is examined in relation to the iron and carbon content of ferromagnetic fly ash fractions. The goal of this research is to evaluate the environmental relevance of the influence of ferromagnetic fractions of fly ash upon

the chemistry of PAH under environmental conditions.

Pyrene is vapor deposited onto the surfaces of such adsorbents as Fe_3O_4 , Fe_2O_3 , five ferromagnetic fly ash fractions, and a nonmagnetic fly ash fraction. These fractions are characterized as to their percentage by weight of iron and carbon. The fly ash samples have been collected from the hoppers of electrostatic precipitator collection devices.

Samples upon which pyrene vapor has been deposited are illuminated by an intense light source that simulates sunlight. The samples, both illuminated and nonilluminated, are subject to solvent extraction by sonication or micro-soxhlet techniques. The extracts are examined to determine if photodecomposition of pyrene occurs. Precautionary measures are taken to minimize thermal degradation of adsorbed pyrene. No attempt is made to identify photochemical products.

2. Actinometry Research

The second objective of this thesis is to determine if chemical actinometry is a viable method for estimating illumination lamp power under the experimental conditions of this laboratory. An attempt is made to determine the average power of the illumination system. An attempt is also made to determine if the lamp power can be adjusted by adjusting the input current of the lamp.

An aqueous actinometer solution of p-nitroanisole and pyridine is illuminated by a xenon 300 W illumination lamp (which is used to illuminate fly ash samples) for a predetermined time. Experimental conditions simulate those for illuminating fly ash samples. The actinometer solution is examined by high performance liquid chromatography before and after illumination to determine the extent of

photochemical reaction. A decrease in the concentration of p-nitroanisole in the solution is assumed to show extent of photochemical reaction.

CHAPTER II

EXPERIMENTAL

A. Fly Ash Research

1. Materials for Fly Ash Research

The PAH utilized for these experiments was pyrene. Pyrene was obtained commercially from Eastman Organic Chemicals.

The adsorbents for this study were two iron oxides, five magnetic fractions of fly ash, and a nonmagnetic fraction of fly ash. The iron oxides examined were Fe_3O_4 and Fe_2O_3 (Alpha Resources, Danvers, Ma.), with stated purities of 99.5 % and 99.9 %, respectively. Kaneb (KA) ash was obtained from McIntosh power plant in Lakeland, Florida. The Texas ash (TX) was obtained from a steam plant burning Texas lignite. The Vince Conrad (VC) stack ashes were provided by Vincent B. Conrad of Consolidated Coal Company, Library, Pa. All of the ashes were collected from the electrostatic precipitators of coal-fired power plants.

The solvents used to extract pyrene from fly ash and other substrates were analytical grade methanol and toluene. Both of these solvents were purchased from S/P Mallinckrodt.

Solvents utilized to dissolve fly ashes for atomic absorption analyses (for iron content) were 10% HF (obtained from Dr. James Adcock), concentrated HCl (Fisher Scientific Company), concentrated HClO_4 (Baker Analyzed Reagent), and concentrated HNO_3 (Mallinckrodt).

2. Size Fractionation of Fly Ash Samples

Each stack ash was first separated into five size fractions (viz., < 45, 45-74, 75-124, 125-149, and > 150 μm) by sieving. The experiments in this study utilized the < 45, 45-74, and 75-124 μm fractions of ash.

3. Separation of Magnetic Particles From Fly Ash Samples

Magnetic fractions were collected from the size fractionated ash utilizing two magnets. First, a large, strongly magnetic horseshoe magnet was utilized to collect all of the magnetic particles. This was accomplished by placing the magnet in a large beaker and moving the beaker and magnet through a sample of ash that was spread out on aluminum foil. The magnetic particles adhered to the bottom of the beaker. These magnetic particles were collected and transferred by holding the beaker and magnet over another piece of foil and removing the magnet from the beaker. This procedure was repeated until no other particles could be collected.

Second, a small stirring bar magnet with weak magnetization was utilized to collect the strongly magnetic particles of ash. This was accomplished by placing the stirring bar magnet in a test tube and moving the tube through the particles that had been collected utilizing the horse-shoe magnet. The strongly magnetic particles stuck to the bottom of the test tube. These particles were transferred to another piece of foil and deposited by removing the magnet from the test tube (the magnet was attached to a string to make this easy). This procedure was repeated until all of the strongly magnetic particles of an ash were

collected. This was the fraction of ash that was utilized as the "iron-enriched" (ferromagnetic) fraction.

4. Iron Determinations in Fly Ash Samples

Magnetic ash fractions and some nonmagnetic ash fractions were examined for their carbon and iron content (% by weight). The fly ash samples were prepared for iron analyses by dissolving approximately 0.1 g of ash in a mixture of 10 ml of each of the following acids: concentrated HCl, concentrated HClO₄, concentrated HNO₃, and 10% HF. Solutions were prepared in Teflon beakers over a heated stirring plate in a hood. The solutions were stirred (with a Teflon coated stirring bar) and heated for up to three days until dissolution of the fly ash was complete. Two ml of HF was added periodically to facilitate complete dissolution. Dissolution was assumed to be complete when no magnetic particles could be seen sticking to the magnetic stirring bar. After dissolution of the ash, the solutions were filtered by gravity filtration through filter paper maintained in a Teflon funnel. The solutions were then diluted to 50 ml with HPLC grade water in a Teflon graduated cylinder, and transferred to Teflon bottles. Standard solutions were prepared by dissolving approximately 1.0 g of Fe₂O₃ in aqua regia over heat and diluting to 100 ml with HPLC grade water. Typical concentrations of the standards were 2862, 1431, 716, 358, 179, and 89 µg/ml in iron, respectively.

The fly ash and iron standard solutions were examined for their iron content by atomic absorption spectrophotometry. The instrument utilized for these analyses was a Varian AA-1475 spectrophotometer. The lamp utilized for these determinations was a "Varian Spectra AA" hollow

cathode lamp for iron analysis. The analyses were conducted at a wavelength of 392 nm. The integration time was set for five seconds. The lamp current and slit were adjusted to 5 mA and 0.2 nm, respectively. An oxidizing flame of air and acetylene was utilized.

A calibration curve, as shown in Figure 2.1 (absorbance units versus $\mu\text{g/ml}$ of iron), was established by atomic absorption analysis of standard solutions of Fe_2O_3 . The concentration of iron ($\mu\text{g/ml}$) in an unknown sample was determined by obtaining the absorbance of the unknown sample and utilizing the calibration curve to determine the amount of iron present. Ten absorbance measurements were made of each sample and the average of each was taken as the absorbance. The percentage of iron present in the unknown sample was inferred by determining the product of the volume (V, in ml) and the concentration (C, in $\mu\text{g/ml}$) of the sample and dividing by the amount of ash dissolved (m, in μg).

$$\% \text{ Fe} = (V)(C)100/m \quad (8)$$

The quantity determined was % iron by weight in each ferromagnetic fly ash fraction.

5. Pyrene Deposition on Substrates

Pyrene was deposited on samples which had been degassed to remove organic residues. Substrates were degassed by passing a steady stream of nitrogen through them for 24 hours while they were being heated (100-200°C). This was done in an degassing cell (adsorption cell) maintained in a heater coil. This apparatus was separate from the PAH deposition apparatus. Samples of adsorbed pyrene were prepared by allowing vapor phase pyrene to adsorb onto the surface of the substrates

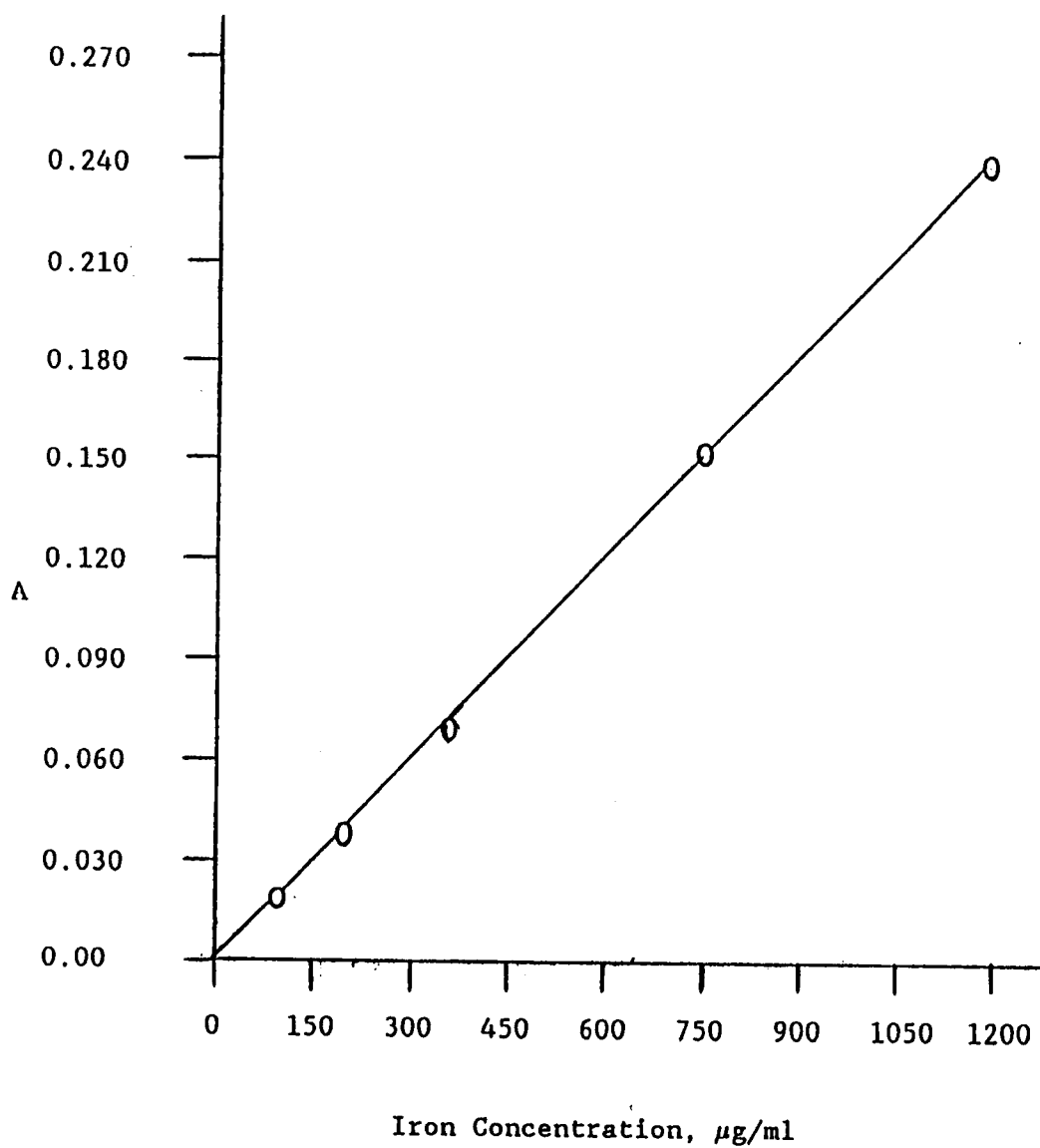


Figure 2.1 Atomic Absorption Calibration Curve for Iron

at 100-200°C. This was to simulate the adsorption process of coal fired plant emissions.^{20,39}

A schematic diagram of the pyrene vapor deposition apparatus is shown in Figure 2.2. This apparatus was composed of two chromatographic ovens; each had its own temperature controller, heater coil, thermocouple, and fan to maintain uniform heat distribution. This apparatus utilized a N₂ carrier gas stream during a deposition.

The first oven contained the PAH generator. The PAH (pyrene) was placed in a removable diffusion tube. The temperature (125°C) of this oven was maintained at a temperature below the melting point of pyrene (156°C). Pyrene in the vapor phase was generated and transported to the second oven (adsorption oven) by the carrier gas. The vapor stream passed through the bed of substrate and was adsorbed on the surface.^{20,39} The PAH generator oven was connected to the second oven by Teflon tubing wrapped in heating tape to maintain the vaporization temperature of the PAH.

The second oven contained the substrate adsorption cell, as seen in Figure 2.3. This removable adsorption cell was connected to the inlet and outlet by self-sealing connectors.²⁰ The temperature of the second oven was maintained at a temperature above the melting point of the PAH (180°C). This oven contained two valves; "valve one", for bypassing the cell or passing PAH through the adsorption cell and substrate; and "valve two", to facilitate transporting the pyrene flow to a flame ionization detector (FID) or detouring the flow of pyrene to the outlet of the adsorption oven. During a deposition the PAH was carried through the substrate in the adsorption cell by the N₂ carrier

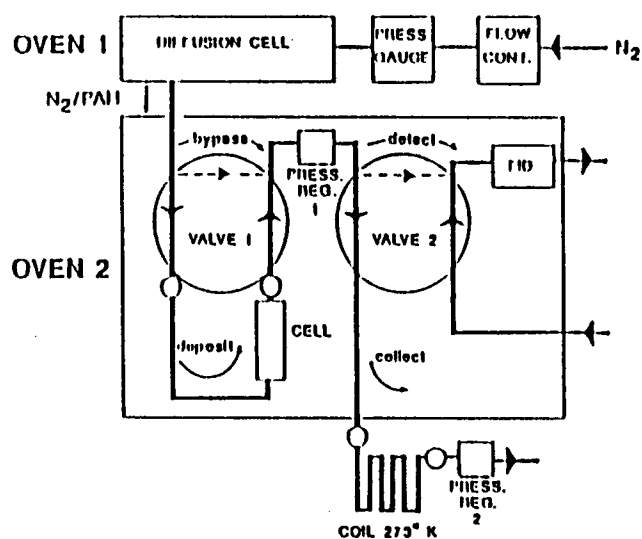


Figure 2.2. Apparatus Utilized for Depositing Vapor Phase PAH on Solid Substrates^{3,20}

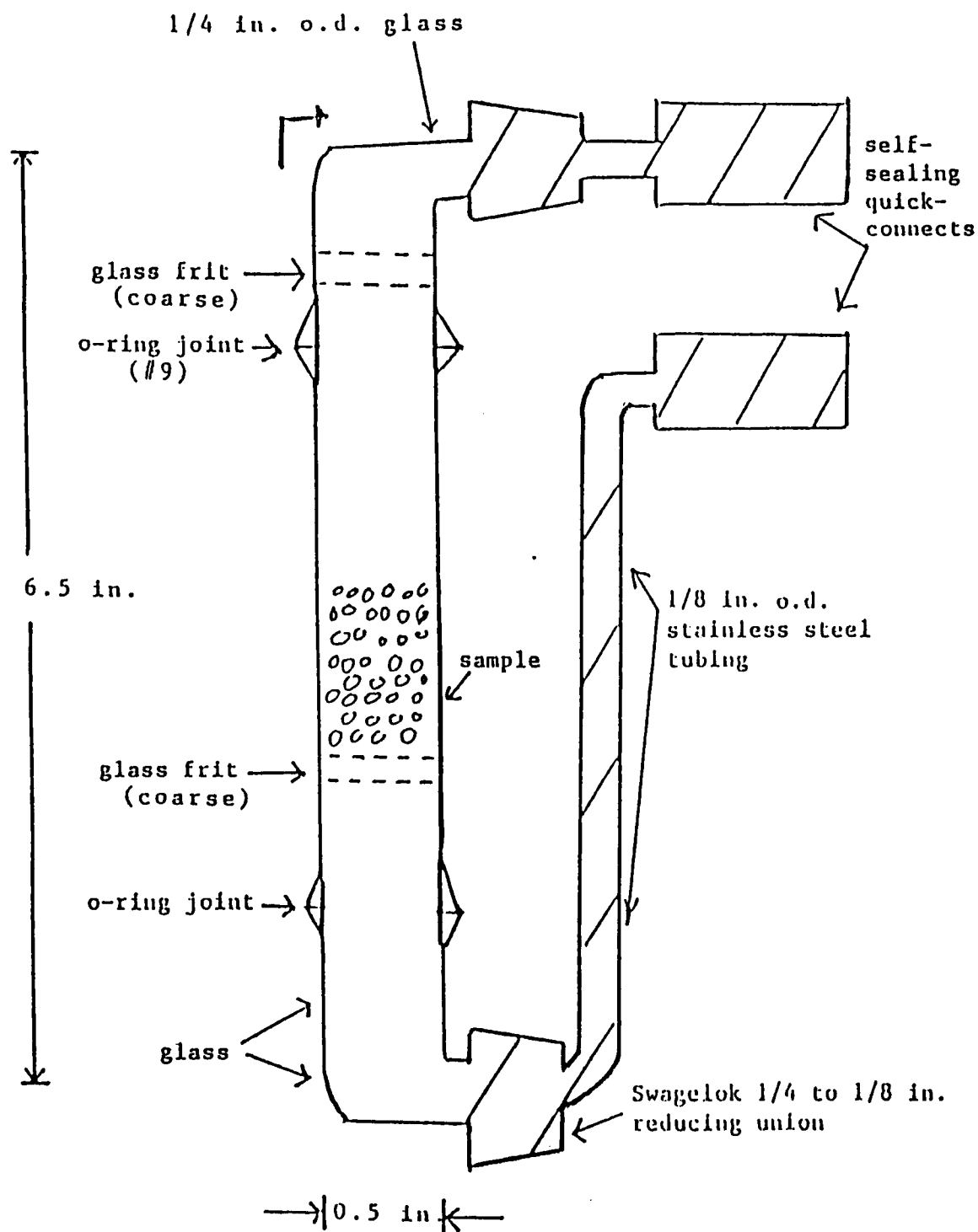


Figure 2.3. Adsorption Cell²⁰

gas and was deposited on the surface. The quantity of PAH being deposited was monitored by the FID connected to a chart recorder. The FID signal was proportional to the amount of PAH flowing to the detector (determined by calibration).

Prior to depositing the PAH, the walls of the adsorption cell were coated with pyrene. This was accomplished by depositing pyrene vapor on the walls of an empty cell in the deposition apparatus, to ensure that adsorption of pyrene was by the fly ash and not the cell walls. This was necessary in order to quantify the amount of pyrene adsorbed by the substrate (as opposed to the quantity of pyrene adsorbed by the substrate and adsorption cell).

After the adsorption cell was coated with pyrene, the substrate was transferred from the degassing cell to the adsorption cell within the confines of a dry box. The adsorption cell with substrate was then connected to the inlet and outlet in the adsorption oven, the oven temperature was allowed to equilibrate at 180°C for 30 minutes, and the deposition was started. This was accomplished by switching "valve one" from the "bypass" to the "through cell" position, allowing the pyrene vapor to permeate the substrate in the adsorption cell. A decrease in the pyrene mass flow rate (in $\mu\text{g}/\text{hour}$), as evidenced by a decrease in the FID signal, occurred as the result of pyrene being adsorbed by the substrate (see Figure 2.4).

The goal of the deposition was to deposit enough pyrene onto the surface of the substrate to obtain a concentration of 100 μg of pyrene per gram of substrate, or to saturate the surface with pyrene, whichever was obtained first. This was accomplished by first determining the mass

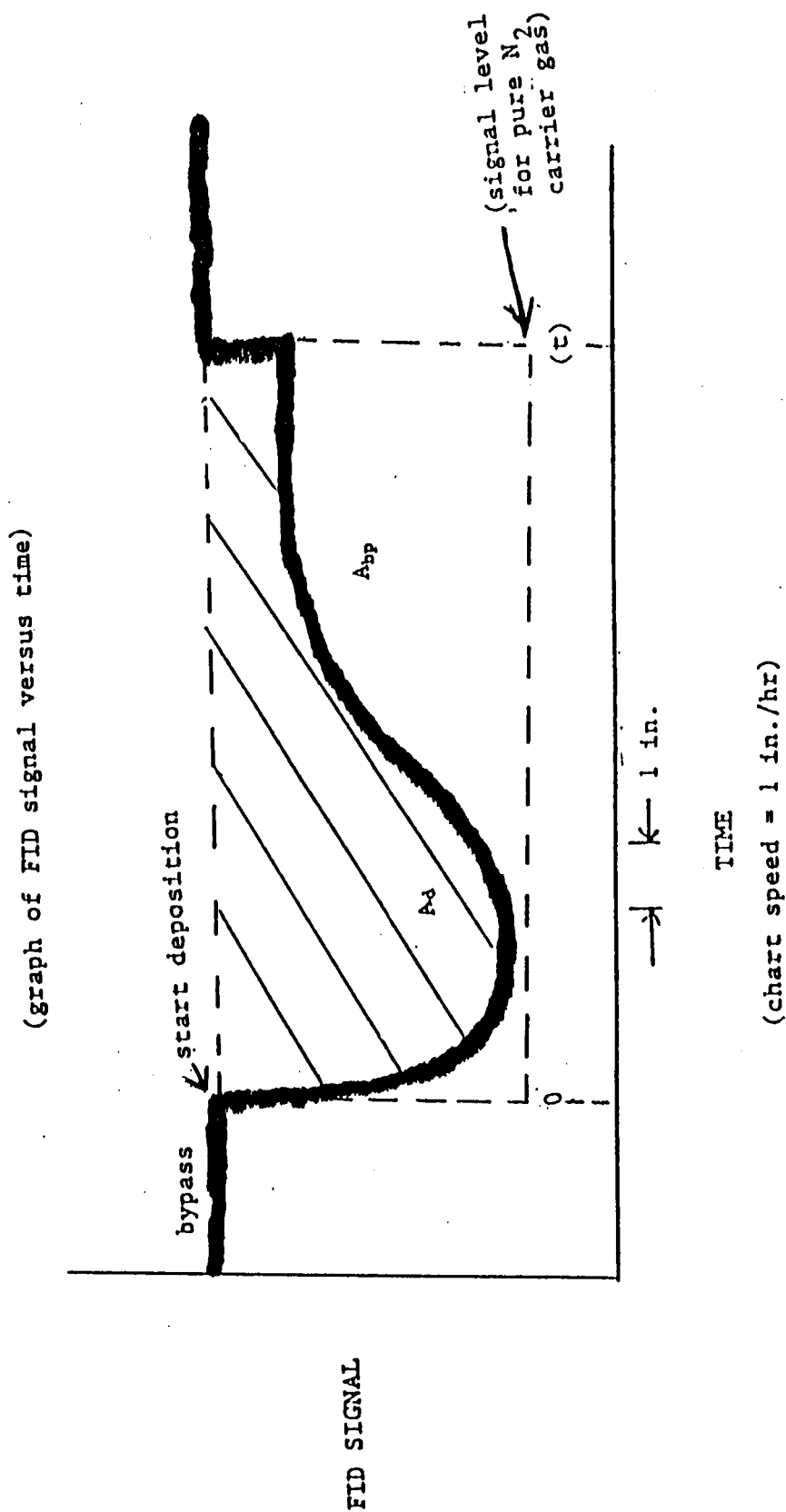


Figure 2.4. Graph of FID Signal (Versus Time) When the Rate of Adsorption of PAH by the Substrate is not constant²⁰

flow rate of pyrene prior to deposition ("valve one" in the "cell bypass" position).

The mass flow rate (in units of $\mu\text{g}/\text{hour}$) of pyrene was calibrated by collecting pyrene for a known amount of time (usually 15 minutes) in a calibration coil (Figure 2.5).²⁰ The calibration coil consisted of a 30 to 40 cm length of 1/8 inch i.d. stainless tubing, which was coiled to fit into an ice bath, with Teflon tubing at the ends providing thermal insulation. The calibration coil was connected to the outlet of the adsorption oven and was maintained in an ice water bath during the collection. Collection of the pyrene was accomplished by moving "valve two" from the "FID" position to the "outlet" position ("valve one" in "bypass" position) which allowed the pyrene to flow to the outlet of the adsorption oven and into the calibration coil. The collection was stopped by switching "valve two" from the "outlet" position to the "FID" position. This process is described in more detail by Engelbach.²⁰

After collection, the calibration coil was immediately detached from the adsorption oven outlet and reattached to a solvent reservoir containing 45 ml of methanol. A pressure of 5 psi of nitrogen was used to force the methanol through the coil and into the flask. Pyrene was washed from the coil into a volumetric flask with methanol, and quantified by uv-visible spectrophotometry.²⁰ A Beer's law plot (absorbance versus pyrene concentration) was determined by uv-visible analysis (Varian Cary 219 UV-visible spectrophotometer) of standard solutions of pyrene dissolved in methanol. Calibration was performed before a deposition in order to determine the initial mass flow rate of pyrene. Calibration was also performed after deposition in order to

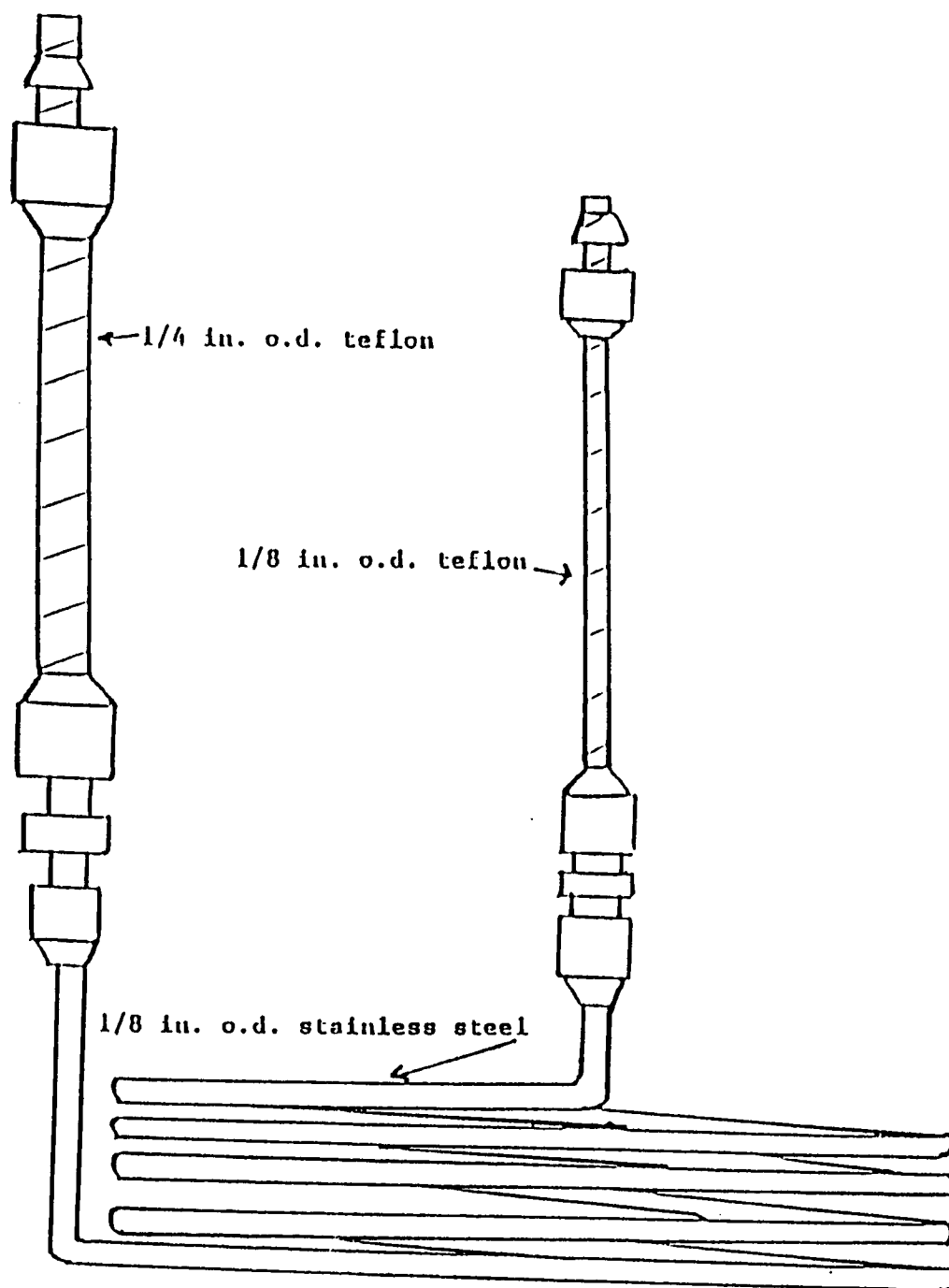


Figure 2.5. Calibration Coil for Collecting and Quantifying the Mass Flow Rate of PAH²⁰

determine if the mass flow rate of pyrene had changed during the deposition. A change in the mass flow rate of pyrene would cause uncertainties in the amount of pyrene adsorbed by the substrate.

The amount of pyrene adsorbed on a sample was estimated from the FID plot (Figure 2.4 and Figure 2.6). First, the total mass of pyrene (M_{Tpyr}) flowing through the adsorbent was inferred by determining the product of mass flow rate with "valve one" in the "cell bypass" position (mfr_{bp}) and total time of deposition (t_d):

$$M_{Tpyr} = (mfr_{bp})(t_d). \quad (9)$$

Second, the fraction of pyrene (X_{pyr}) adsorbed by the substrate was determined by dividing the area of the deposition curve (A_d) by the area of the curve when "valve one" was in the "cell bypass" position (A_{bp}) (see Figure 2.4).

$$X_{pyr} = A_d/A_{bp} \quad (10)$$

The amount of pyrene adsorbed by the substrate (M_{subpyr}) was then determined from the product of the fraction of pyrene adsorbed and the total mass of pyrene flowing through the adsorption cell:

$$M_{subpyr} = X_{pyr} \times M_{Tpyr}. \quad (11)$$

Finally, the adsorbate concentration (C) was calculated by the equation:

$$C = M_{subpyr}/m \quad (\text{units of } \mu\text{g/g}) \quad (12)$$

where m was the mass of substrate.

If the affinity of the surface of the substrate for pyrene was virtually constant (amount of pyrene adsorbed per unit time was virtually constant throughout deposition), as in Figure 2.6, the amount of pyrene adsorbed by the substrate in a given amount of time was easily estimated. This was useful in order to deposit a predetermined amount

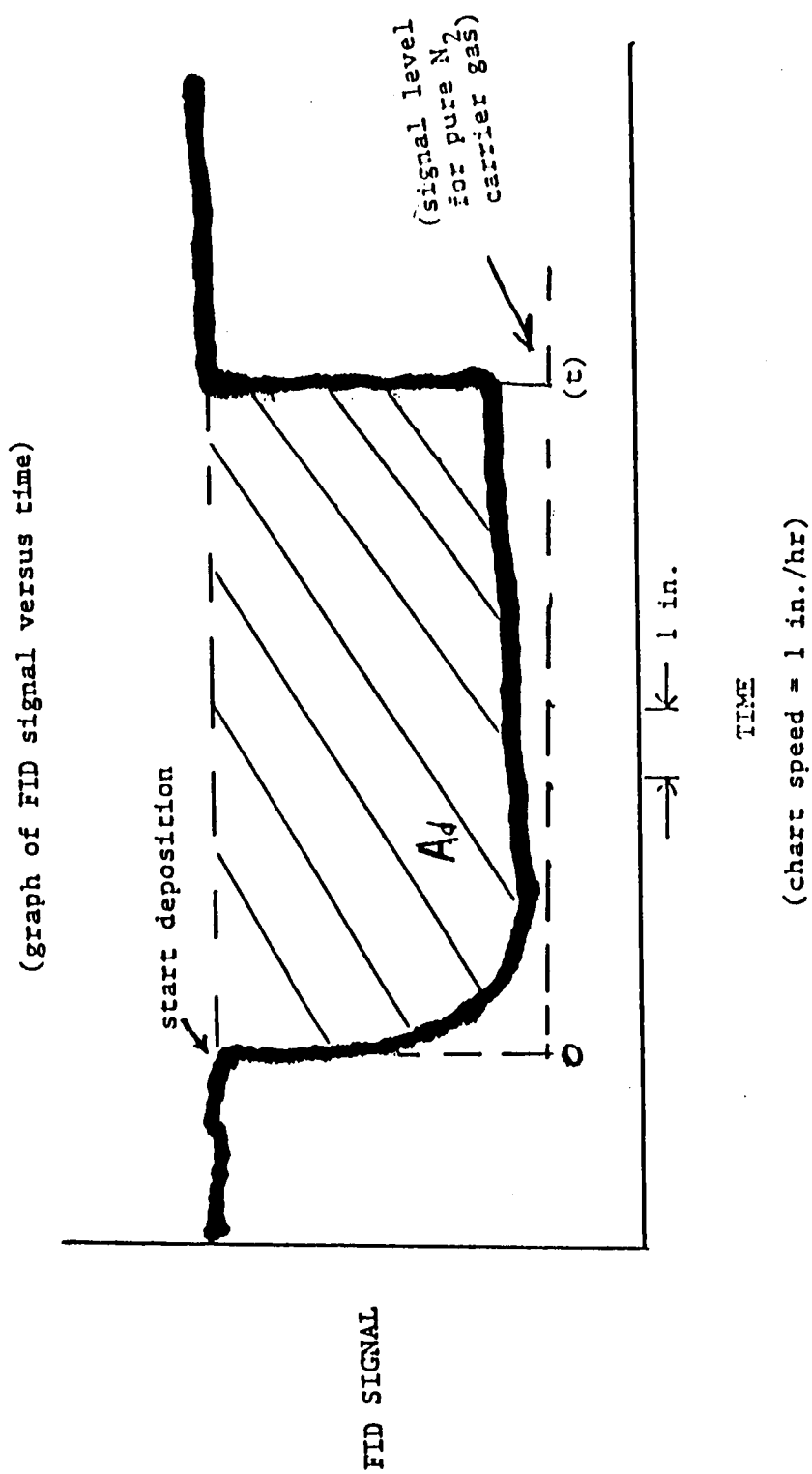


Figure 2.6. Graph of Deposition of Substrate in the Case When Rate of Adsorption of PAH is Constant

of pyrene on the surface of the substrate. If the affinity of the surface of the substrate for pyrene was not constant, as in Figure 2.4 (amount of pyrene adsorbed per unit time decreases as the affinity of pyrene for the surface of the substrate decreases), it was difficult to predetermine the amount of pyrene that would be adsorbed by a particular substrate in a given amount of time.

6. Illumination of Samples

After deposition of pyrene, the sample was mixed for one hour (in a sample bottle attached to a rotary mixer) to obtain uniformity and the photodecomposition of pyrene adsorbed on the surface of the substrate was investigated. A portion of the sample was placed in a sample bottle wrapped in aluminum foil and kept in the dark for at least 24 hours. A second portion of the sample (0.06-0.25 g) was illuminated in a rotary quartz cell using a Cermax LX300 xenon illuminator. The sample and cell were aligned in the center of the light beam at a distance of 38 cm from the illumination source and illuminated for 24 hours. A rotary evaporator continually rotated the cell (60 cycles per minute) during the illumination to ensure that all of the sample was exposed.

The infrared radiation output of the irradiation lamp was filtered by a cell to decrease the probability of thermolysis of pyrene. This cell was 20 cm long and was filled with distilled water, which filters out much of the near-infrared radiation produced by the xenon lamp. The windows of the cell were made of quartz to allow uv-visible radiation to pass through and illuminate the sample (see Figure 2.7). The cell was kept cool by a water jacket.

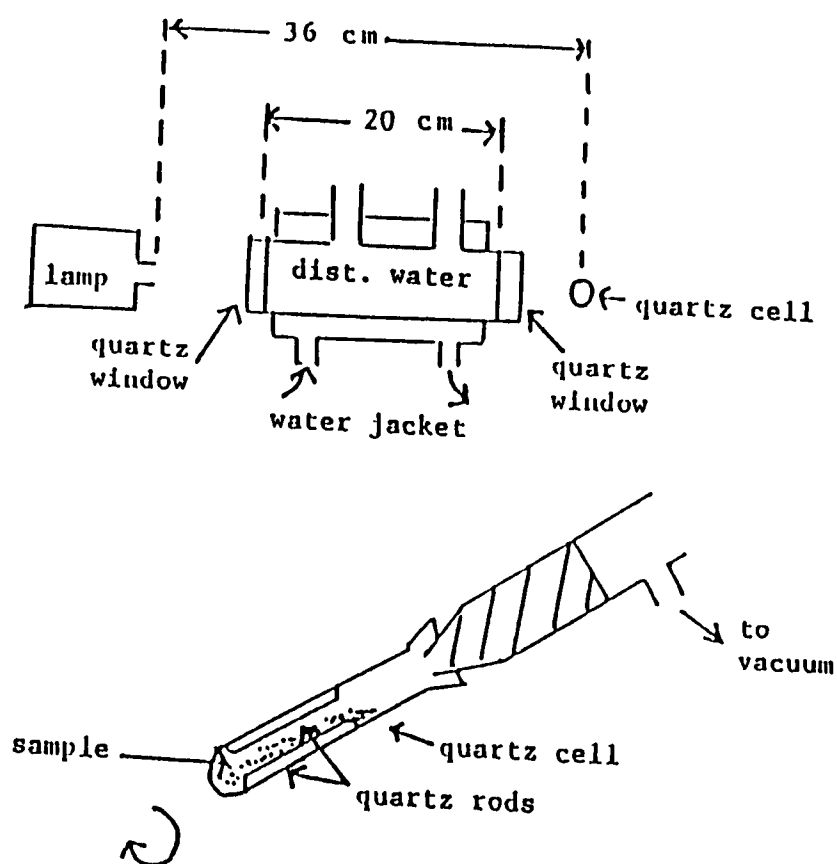


Figure 2.7. Fly Ash Illumination Apparatus^{20,39}

7. Extraction and Analysis of Samples

The pyrene content of the illuminated sample was compared with that of the unilluminated sample (dark sample). The difference in pyrene content between illuminated and unilluminated samples was presumed to show the amount of photodecomposition. No attempt was made to identify the photochemical products that may have been produced.

The samples were prepared for quantitative analysis of pyrene either by micro-soxhlet extraction in methanol or by sonication extraction in toluene. It was necessary to extract the pyrene from the substrates because direct determination of organic compounds adsorbed on fly ash is difficult (due to the complex structure of fly ash).

Samples that were to be extracted by the micro-soxhlet technique were prepared by weighing out approximately 0.0250 g of substrate (to the nearest 0.001 g) into a cellulose extraction thimble (Whatman). Four samples each of illuminated and unilluminated substrate were prepared for micro-soxhlet extraction. Samples were extracted in methanol in a micro-soxhlet apparatus for 24 hours. After extraction, each of the extracts was transferred to a 50-ml volumetric flask and diluted to 50 ml with methanol.

Samples that were to be extracted by sonication were prepared by weighing out approximately 0.0250 g of substrate into a 25-ml volumetric flask and then adding approximately 20 ml of toluene to the flask. Four samples each of illuminated and unilluminated ash were prepared. The samples were sonicated in a water bath, utilizing a Branson 2200 sonicator, for 90 minutes at 60°C. All eight solutions were sonicated simultaneously in the same bath. After sonication, the extracts were

diluted to 25 ml with toluene. No attempt was made to remove the substrate from the extraction solution.

Irrespective of which extraction procedure was used, the extracts were transferred by disposable pipet into a quartz uv-visible cell (path length was 1.00 cm) and examined for their quantity of pyrene by uv-visible spectrophotometry (Varian Cary 219 spectrophotometer). Each spectrum was scanned over the range of 380-320 nm and the concentration of pyrene in each solution determined utilizing a calibration curve that was obtained using pyrene solutions of known concentrations. From these concentrations, the known volume of the solutions, and the known initial weight of substrate, the concentration of pyrene extracted (μg of pyrene per gram of substrate) could be determined. As stated earlier, a difference in quantity of pyrene between the illuminated (m_t) sample and the unilluminated (m_o) sample was presumed to show the percentage photodecomposition; high performance liquid chromatographic analysis of extracts in which photodecomposition was not evident, showed that no substances (interferents) other than pyrene were present.

$$\% \text{ Photodecomposition} = [(m_o - m_t)/m_o] \times 100 \quad (13)$$

B. Actinometry Using a p-Nitroanisole/Pyridine Actinometer

1. Materials for PNA/PYR Actinometry Research

P-Nitroanisole (PNA, practical grade) and p-nitrotoluene (PNT, practical grade) were obtained commercially from Kodak Chemicals. Reagent grade pyridine (PYR) and HPLC-grade acetonitrile were purchased from Fisher Scientific Company. HPLC-grade water was purchased from American Burdick and Jackson.

2. Preparation of the Actinometer and Internal Standard Solutions

A PNA stock solution was prepared by dissolving 0.2010 g of PNA in 250 ml of acetonitrile and diluting to 1000 ml with HPLC-grade water in a volumetric flask (PNA is not readily dissolved in water). The PNA concentration of this solution was $1.313 \times 10^{-3} \text{ M}$.

A PYR stock solution was prepared by dissolving 1.0837 g of PYR in HPLC-grade water and diluted to 1000 ml in a volumetric flask. The PYR concentration of this solution was $1.370 \times 10^{-2} \text{ M}$.

An actinometer solution was prepared just prior to illumination by utilizing a volumetric pipet to transfer 2.00 ml each of the PNA and PYR stock solutions to a 50-ml volumetric flask and diluting to 50 ml with HPLC grade water. This solution had a concentration of $5.25 \times 10^{-5} \text{ M}$ PNA, $5.48 \times 10^{-4} \text{ M}$ PYR, and was 1% acetonitrile by volume. The solution was mixed thoroughly and kept in the dark when not in use.

PNT was utilized as the internal standard for the HPLC determination of the concentration of PNA in solution. The PNT stock solution was made by dissolving 0.0502 g of PNT in 100 ml of acetonitrile and diluting to 1000 ml with HPLC-grade water in a volumetric flask. The concentration of the PNT stock solution was $3.66 \times 10^{-3} \text{ M}$. One ml of this solution was transferred to a 100-ml volumetric flask via 1.00-ml volumetric pipet and diluted to 100 ml with HPLC grade water. This solution was $3.66 \times 10^{-5} \text{ M}$ PNT in 1% acetonitrile.

3. Illumination of the Actinometer

Three ml of the actinometer solution was transferred to a quartz uv-visible spectrophotometer cell (1.00 cm path length) utilizing a

3.00-ml volumetric pipet. The sample and cell (placed in a cell holder) were aligned in the center of the light beam 38 cm from the illumination source on an optical bench. The cell holder was utilized to set the alignment such that the actinometer solution was exposed to the most intense part (the center) of the light beam (Figure 2.8).

After the proper alignment was established, the cell was placed in the cell holder and illuminated for a known amount of time. A stopwatch was utilized to determine the time of illumination and a shutter was utilized to start and stop the illumination of the actinometer sample. The lamp was left on continuously during the illumination experiments.

4. Analysis of the Actinometer Solution by HPLC

After illumination, the actinometer solution was prepared for high performance liquid chromatographic (HPLC) analysis. The actinometer solution was transferred to a 5.00-ml volumetric flask which contained 0.50 ml of $3.66 \times 10^{-5} \text{ M}$ of PNT (internal standard). The cell was washed twice with 1% aqueous acetonitrile and these washings were also transferred to the flask to insure that all of the actinometer solution had been collected. The solution was diluted to 5.00 ml with 1% aqueous acetonitrile solution. The concentration of an unilluminated solution was $3.15 \times 10^{-5} \text{ M}$ PNA, $3.29 \times 10^{-4} \text{ M}$ PYR, $3.66 \times 10^{-6} \text{ M}$ PNT, and was 1% in acetonitrile by volume.

Three standard solutions were prepared to obtain a calibration curve. The concentrations of PNA in the standard solutions were; (1) $3.15 \times 10^{-7} \text{ M}$ PNA, (2) $3.15 \times 10^{-6} \text{ M}$ PNA, and (3) $3.15 \times 10^{-5} \text{ M}$ PNA,

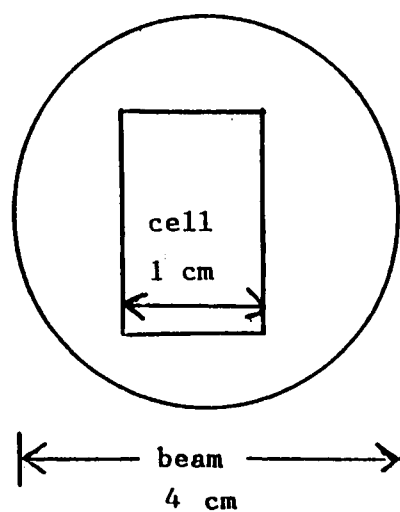
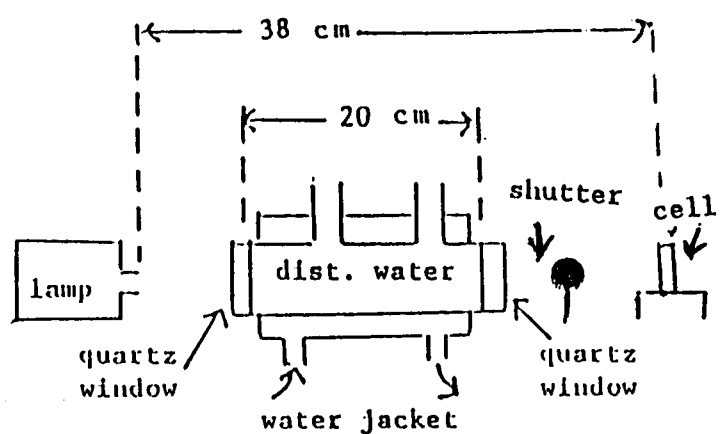


Figure 2.8. Apparatus for Illumination of Actinometer Solution

respectively. Each standard solution contained 3.66×10^{-6} M PNT as the internal standard.

After illumination, the actinometer solution was examined by HPLC (Varian 5000 liquid chromatograph with 10 μ l injector) utilizing a reverse phase column (Vydac reverse phase C₁₈ column, 25 cm long) and a multiwavelength uv-visible detector (Varian 2050 variable wavelength detector). The internal standard method was the method of quantification. The determinations were obtained by utilizing a Varian 4270 integrator which was connected to the detector. The detector was set at 310 nm. The flow rate was set at 1.5 ml/min, and the carrier solvent was 50% aqueous acetonitrile. The retention times of the PNA and PNT were 3.00 min and 3.77 min, respectively (see chromatogram, Figure 2.9).

Calibration and determination of the solutions was by peak area (in mV). The quantity determined was the amount of PNA (μ mol/l) remaining in solution. A calibration curve was established from the standard solutions by making three injections of each solution. After the calibration curve was established, standard solutions were injected and quantified. Standard solutions were analyzed before and after analysis of the illuminated samples. This was done to ensure that the detector was stable and that the determinations of PNA concentration in solution were accurate.

Inasmuch as the stoichiometry of the actinometer reaction is 1:1 (PNA:product), the number of molecules of photochemical product formed (n_p) was easily determined by quantifying the amount of PNA present

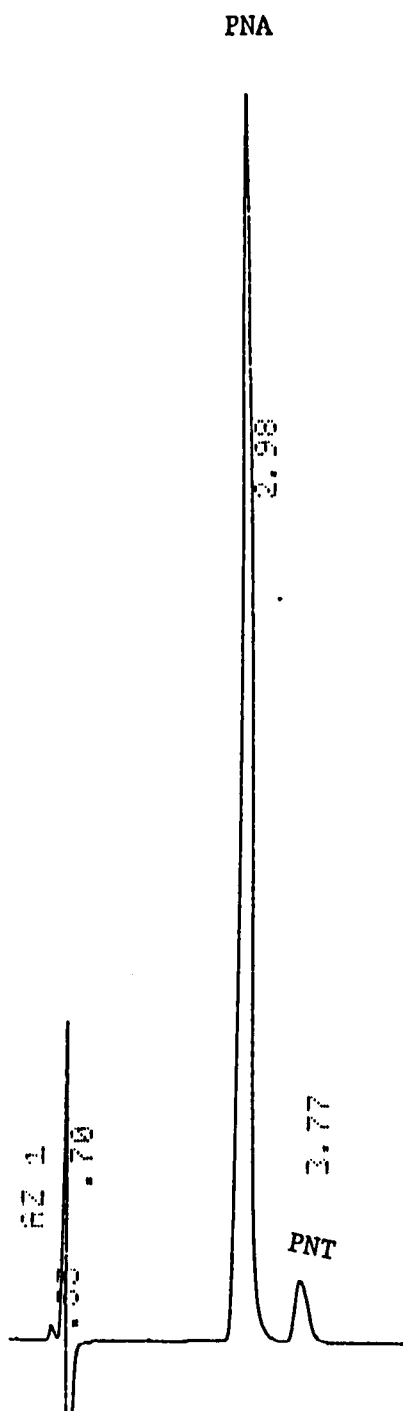


Figure 2.9. Liquid Chromatogram of Actinometer Solution

before and after exposure to radiation. Then, n_b could be substituted into Equation 7 (p 12).

5. Calculations used in Chemical Actinometry

Chemical actinometers are, with few exceptions, used to determine the power (or intensity) of monochromatic light only. These determinations are relatively easy, inasmuch as the output of the lamp and the absorbance of the actinometer are constant when utilizing a monochromatic light source. The absorbance of the actinometer is substituted directly into Equation 7 (p 12) to determine the power of the illumination lamp.

It is much more difficult to determine the power of polychromatic light. The absorbance of the actinometer, as well as the output (emission) of the illumination lamp, varies as a function of wavelength. This must be accounted for in order to determine the power (or intensity) of a polychromatic light source. This is accomplished by determining the average absorbance (A_a) of the actinometer over the wavelength range in which the absorbance spectrum of the PNA/PYR actinometer coincides with the emission spectrum of the illumination lamp. The average absorbance is the value that is substituted into Equation 7 (p 12) to determine the power of the illumination lamp.

The objective of the actinometer studies was to determine the power emitted by the xenon lamp (used to illuminate fly ash samples) over the range of 410 nm to 220 nm. This measurement requires that average absorbance of the actinometer solution over the wavelength range of the absorbance spectrum be determined. The wavelength range of 410-220 nm was selected because it was the range in which the absorption

spectrum of the actinometer solution coincided with the emission spectrum of the lamp. The absorbance of the actinometer was obtained in 10-nm intervals experimentally by absorption spectrophotometry (see the uv absorption spectrum of the PNA/PYR actinometer solution in Figure 2.10).

At 10-nm intervals, the absorbance (A_k) of the actinometer solution was multiplied by the relative output (P_k), of the illumination lamp. These values were summed to obtain the total rate of photon absorption by the actinometer ($P_k A_k$, as shown in Table I). This was done to account for the fact that absorbance of the actinometer solution and the lamp output vary as a function of wavelength. The average rate of absorption of photons (A_a) by the actinometer solution was determined from the following equation (number of 10-nm intervals (N) from 410-220 nm is 20).

$$A_a = (\sum P_k A_k) / 20 \quad (14)$$

The relative output (P_k) of the illumination lamp at each 10-nm interval was determined by a series of mathematical conversions and calculations (this procedure is detailed in the Appendix). The output of the illumination lamp (P_i , in units of W/nm) at each interval was determined from the emission spectrum shown in Figure 2.11 (obtained from the manufacturer). The highest output of the xenon illumination lamp was at 320 nm ($P = 0.52$ W/nm). The relative output was determined at each 10-nm interval by dividing the output, in watts (W/nm converted to W by multiplying the output of the lamp by the wavelength of emission (λ_i)), at each interval by the output at 320 nm. The relative output at each interval was determined from the following equation.

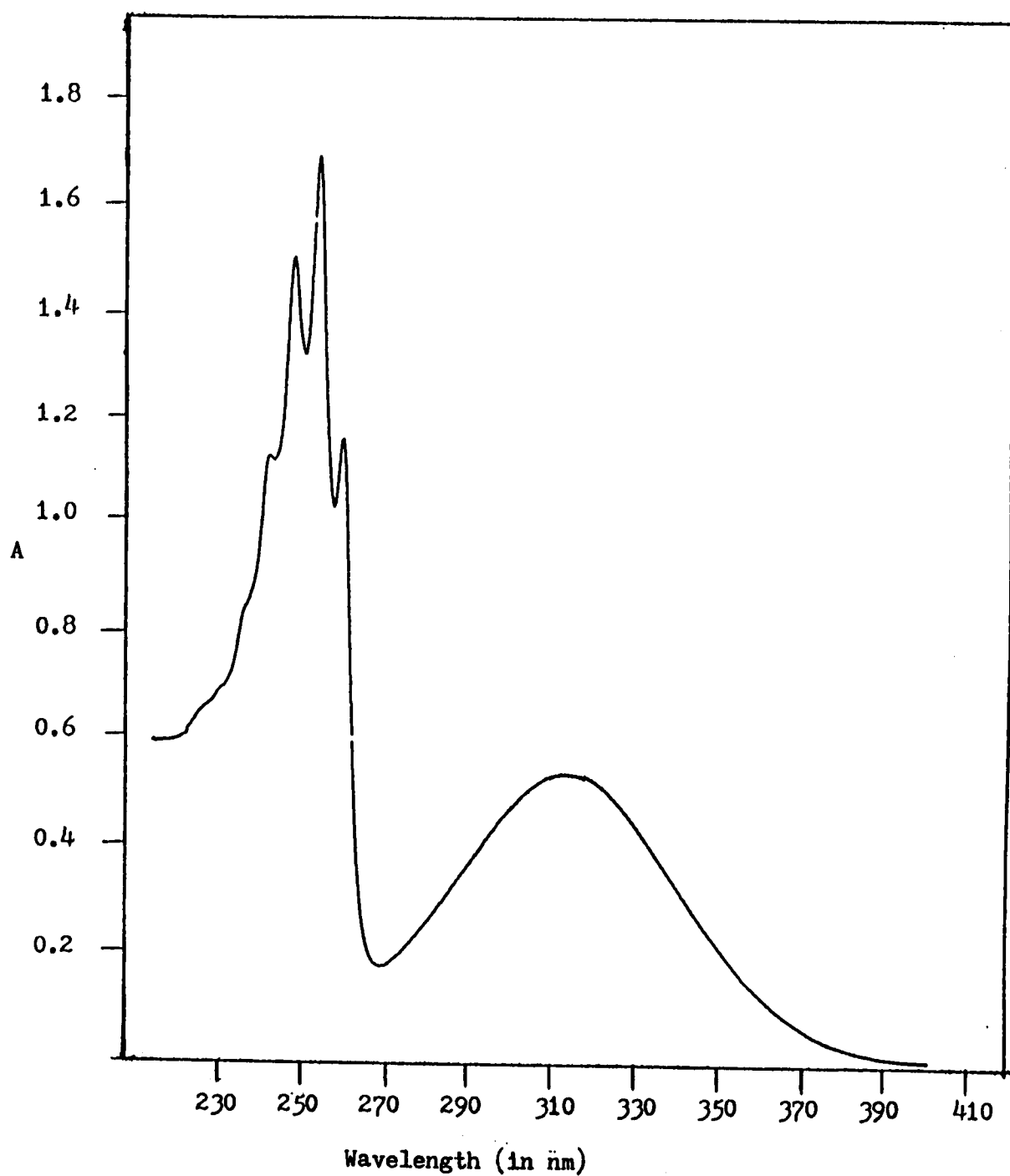


Figure 2.10. Absorption Spectrum of PNA/PYR Actinometer Solution

TABLE I
Determination of the Average Absorbance of
the Actinometer Solution

λ (nm)	A_k of Actinometer Solution (abs.)	P_k of Illumination Lamp	$A_k P_k$
220	0.45	0.17	0.08
230	0.59	0.29	0.17
240	0.70	0.52	0.36
250	1.09	0.63	0.69
260	1.53	0.79	1.21
270	0.61	0.74	0.45
280	0.18	0.76	0.14
290	0.28	0.75	0.21
300	0.39	0.82	0.32
310	0.50	0.85	0.42
320	0.55	1.00	0.55
330	0.52	0.93	0.48
340	0.43	0.93	0.40
350	0.31	0.96	0.30
360	0.20	0.93	0.19
370	0.11	0.98	0.11
380	0.05	1.07	0.05
390	0.03	1.10	0.03
400	0.01	1.15	0.01
410	0.00	1.20	0.00

$$A_a = (\Sigma A_k P_k) / 20$$

$$A_a = 0.31$$

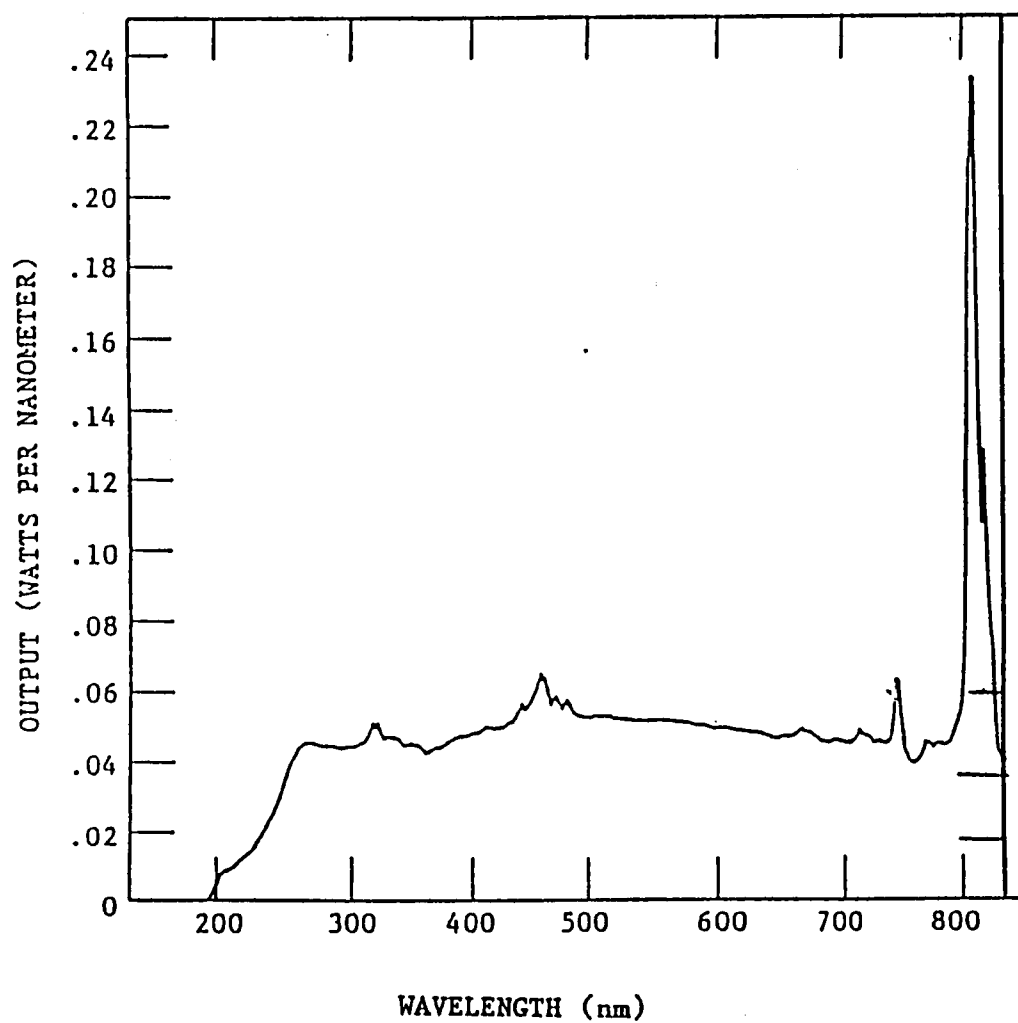


Figure 2.11. Cermox Lamp Output (Manufacturers' Data)³⁹

$$P_k = (\lambda_i \times P_i) / (320 \text{ nm} \times 0.52 \text{ W/nm}) \quad (15)$$

P_k was then be substituted into Equation 14 (p 40) to determine A_a .

The quantum yield (Φ_b) of the PNA/PYR actinometer was dependent upon the concentration of pyridine.³⁸ The quantum yield was determined from the following equation.

$$\Phi_b = 0.44[\text{PYR}] + 0.00028 \quad (16)$$

The power of the illumination lamp was determined from the known values of illumination time (t , in sec), average absorbance of the actinometer solution (A_a), amount of photochemical product formed (n_b), and the quantum yield (Φ_b) of the actinometer. These values were substituted into the actinometry equation (Equation 7, p 12) and the power of the illumination was determined. Power can be converted to intensity by dividing the power of the illumination source by the surface area of the sample exposed to illumination (this conversion procedure is described in the Appendix).

CHAPTER III

RESULTS AND DISCUSSION

A. Fly Ash and Pyrene

1. Iron and Carbon Contents of Fly Ash Samples

Table II contains data for the iron and carbon content in iron oxide and fly ash substrates. Five ferromagnetic ash fractions and two nonferromagnetic ash fractions were analyzed by atomic absorption spectrophotometry. The amount of iron and carbon present in a sample is expressed as percentage by weight. The data in Table II show that the amount of iron present in a ferromagnetic fraction varies with the particular fly ash. The two ferromagnetic fractions of Kaneb (KA) ash had the highest percentage of iron. All ferromagnetic fractions of ash examined in this study contained greater than 20% iron by weight.

Two nonferromagnetic ash fractions were also analyzed to determine the amount of iron present (VC67981 and VC68159). This was done in order to determine if the procedure for collecting ferromagnetic particles produced a fraction of ash that was enriched in iron, relative to the amount of iron present in a nonferromagnetic fraction of ash. The ferromagnetic and nonferromagnetic fractions of Vince Conrad ash from power plant # 68159 contained 27% and 7% iron, respectively. The ferromagnetic and nonferromagnetic fractions of Vince Conrad ash from power plant # 67981 contained 24% and 9% iron, respectively. Hence, from the data in Table II, it may be concluded that the ferromagnetic

TABLE II
Percent By Weight of Iron and Carbon
In Substrates

Name of Substrate	Designation	Particle Size μm	% Fe	% C
Fe_3O_4	F	< 45	72	0.00
Fe_2O_3	N	< 45	70	0.00
KA	F	45-74	51	0.57
KA	F	75-124	44	0.64
VC67981	F	< 45	24	7.17
VC67981	N	< 45	9	na
VC68159	F	< 45	27	5.10
VC68159	N	< 45	7	18.8
TX	F	75-124	36 ^a	0.15 ^a

^aData provided by T. D. J. Dunstan.

na - not available.

F - ferromagnetic.

N - nonferromagnetic.

Carbon analyses performed by Galbraith Laboratories,
Knoxville, TN.

Values for Fe_3O_4 and Fe_2O_3 are theoretical and experimental
values.

fractions of ash were enriched in iron relative to the nonferromagnetic fractions.

The determination of the amount of iron in a ferromagnetic fraction of ash is important in order to ascertain if the presence of iron has an affect on the photochemistry of adsorbed PAH. The two iron oxides and all of the ferromagnetic fractions of fly ash in this study contain a sufficient amount of iron ($> 20\%$) to have a possible effect on photochemistry of adsorbed PAH.

The carbon analyses were performed in order to determine if there was a sufficient amount of carbon present in the ferromagnetic fraction of ash to stabilize surface adsorbed pyrene to photodecomposition. The two ferromagnetic fractions of Kaneb ash and the ferromagnetic fraction of Texas ash contained very little carbon ($< 1\%$). The two ferromagnetic fractions of Vince Conrad ash contained less than 10% carbon. The carbon analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

2. Deposition and Extraction of Pyrene on Substrates

The goal of the deposition was to deposit enough pyrene on the surface of the adsorbent to obtain a concentration of $100\text{ }\mu\text{g}$ of pyrene per g of adsorbent, or to saturate the surface of the substrate with pyrene (in order to be able to extract enough pyrene to be within the limit of detection for absorption spectrophotometry), whichever was obtained first. Figure 2.4 (p 25) shows the FID plot of a deposition in which the surface of the ash (Kaneb ferromagnetic ash, $75\text{-}124\text{ }\mu\text{m}$) was becoming saturated with pyrene. This was assumed to show that the strongest adsorption sites of the substrate had been deposited with

pyrene. The affinity of the surface of the ash for pyrene decreases (the amount of pyrene adsorbed per unit time decreases, determined from FID plot) as the number of adsorption sites available on the surface of the ash decreases. The two ferromagnetic fractions of Kaneb ash adsorbed pyrene in this manner. In these cases, the concentration of pyrene on the surface of the adsorbent was estimated from known values of mass flow rate, fraction of pyrene adsorbed (determined from FID plot), length of time for deposition, and weight of adsorbent, via the method discussed in Chapter 2.

Figure 2.6 (p 28) shows the FID plot of a deposition in which the affinity of the adsorbent for pyrene is virtually constant (amount of pyrene adsorbed per unit is virtually constant throughout deposition, from FID plot). This is assumed to show that the surface of the substrate is not becoming saturated with pyrene. This also shows that the surface of the ash is relatively homogeneous. The iron oxides and two of the Vince Conrad ashes (VC68159 ferromagnetic and nonferromagnetic fractions) adsorbed pyrene in this manner. In the case in which the affinity of the ash for pyrene was virtually constant, the amount of time needed to deposit 100 μg of pyrene per gram of adsorbent could be estimated from known values of mass flow rate, weight of adsorbent, and the fraction of pyrene being adsorbed (from FID plot).

Samples of degassed substrate were weighed in a dry box and transferred to an adsorption cell. Then the surface of the substrate was deposited with pyrene from the vapor phase in the deposition apparatus. After deposition, pyrene was extracted from the surface of the substrate (which had been stored in a desiccator) and quantified.

The purpose of these measurements was to determine the amount of pyrene adsorbed on the surface of the substrate, and the amount of pyrene that could be extracted relative to the amount adsorbed. The results of the deposition and extraction of substrates (iron oxides and fly ashes) are shown in Table III. From these data it was concluded that not all of the pyrene adsorbed on the surface of fly ash and iron oxide adsorbents could be extracted. It was also concluded that the amount of pyrene that could be extracted relative to the amount adsorbed varied with the particular substrate.

The fraction of pyrene adsorbed on the surface of the adsorbent (X_{ads}) is defined as amount of pyrene adsorbed by the adsorbent divided by the total amount of pyrene flowing through the bed of adsorbent (Equation 9, p 27). If the affinity of the surface of the ash for pyrene (amount of pyrene adsorbed per unit time) was virtually constant (as in Figure 2.6, p 29), the fraction of pyrene adsorbed is equal to the amount of pyrene adsorbed per unit time (hour) by the substrate, divided by the mass flow rate of pyrene. The fraction of pyrene adsorbed by the adsorbent, under reproducible conditions, may give some idea of the affinity of pyrene for the surface of the adsorbent. The fraction of pyrene adsorbed varied from 27 % for the ferromagnetic fraction of Kaneb ash (size 45-74 μm) to 85 % for the "Vince Conrad" ash fractions, # 68159 (Table III). This suggests that some substrates adsorb pyrene more strongly than others.

Extraction efficiency (Rec, percentage recovery) is defined as the concentration ($\mu\text{g/g}$) of pyrene extracted from the nonilluminated adsorbent divided by the concentration of pyrene deposited on the

TABLE III

Fraction of Pyrene Adsorbed by Substrate, Surface
Coverage of Substrate, Amount of Pyrene
Extracted, and Recovery

Adsorbent	Type	MFR $\mu\text{g}/\text{hour}$	X_{abs}	Surface Coverage, $\mu\text{g}/\text{g}$	Amount of Pyrene Extracted, $\mu\text{g}/\text{g}$	Rec, %
Fe_3O_4	F1	44	0.83	100	$59 \pm 3^{\text{m}}$	59
Fe_2O_3	N1	26	0.61	100	$38 \pm 1^{\text{m}}$	38
VC68159	F1	30	0.85	100	$19 \pm 2^{\text{s}}$	19
VC68159	N1	39	0.85	217	$94 \pm 10^{\text{s}}$	43
KA	F3	10	0.61	33	$23 \pm 3^{\text{m}}$	70
KA	F2	89	0.27	76	$35 \pm 1^{\text{s}}$	46
VC67981	F1	83	na	na	$358 \pm 6^{\text{s}}$	na
TX	F3	na	na	na	$22 \pm 1^{\text{s}, \text{a}}$	na

^aData provided by T. D. J. Dunstan.

MFR - mass flow rate of pyrene.

F1 - ferromagnetic with particle size $< 45 \mu\text{m}$.

F2 - Ferromagnetic with particle size 45-74 μm .

F3 - Ferromagnetic with particle size 75-124 μm .

N1 - Nonferromagnetic with particle size $< 45 \mu\text{m}$.

Rec, % - ((amount extracted/amount adsorbed) x 100).

X_{abs} - Fraction of pyrene in vapor phase adsorbed by substrate.

na - not available.

^mExtracted by micro-soxhlet in methanol.

^sExtracted by sonication in toluene.

adsorbent (surface coverage). The extraction efficiency gives some idea of how strongly pyrene is retained when adsorbed on the surface of the substrate. The extraction efficiency was different for different adsorbents. The highest extraction efficiency observed was 70 % for the ferromagnetic fraction of Kaneb ash (size 75-124 μm). The lowest extraction efficiency observed was 19 % for the ferromagnetic fraction of Vince Conrad ash from power plant # 68159 (size < 45 μm). These observations suggested that there were some very strong adsorption sites on the ashes and that not all of the pyrene was extracted. If this was the case, then the amount of extractable pyrene may be dependent upon the amount of pyrene deposited. Presumably, pyrene would adsorb preferentially on the strongest adsorption sites. Pyrene adsorbed on these strong adsorption sites may be very difficult to extract.

3. Apparent Photodecomposition of Pyrene Adsorbed on Substrates

Approximately one gram (0.5 g when the amount of sample available was small) of a substrate was degassed with nitrogen for 24 hours at 100-200°C. Then the surface of the sample was deposited with pyrene to obtain a concentration of 33-217 μg of pyrene per gram of adsorbent. A portion of this sample (0.06-0.25 g) was placed in an irradiation cell and illuminated and rotated for 24 hours. A second portion was placed in a sample bottle that was covered with aluminum foil and kept in the dark for at least 24 hours. These samples were then extracted to obtain values for both the illuminated and the unilluminated (dark) samples.

Table IV contains data for the apparent photodecomposition and reactivity of pyrene adsorbed on iron oxides and ferromagnetic fly ash substrates. The percentage of photodecomposition for each sample was

TABLE IV

Photochemical Decomposition of Pyrene on Iron Oxides
and Ferromagnetic Fractions of Fly Ash

Adsorbent	Type	Initial [Pyrene], $\mu\text{g/g}$	Final [Pyrene], $\mu\text{g/g}$	% Change
Fe_3O_4	F1	59 ± 3	58 ± 3	2
Fe_2O_3	N1	38 ± 1	37 ± 2	3
VC68159	F1	19 ± 2	19 ± 0	0
VC68159	N1	94 ± 10	92 ± 14	2
KA	F3	23 ± 3	23 ± 2	0
KA	F2	35 ± 1	33 ± 3	6
VC67981	F1	358 ± 6	223 ± 24	38
TX	F3	22 ± 1^a	19 ± 2^a	15^a

^aData provided by T. D. J. Dunstan.

Initial [Pyrene] = concentration of pyrene extracted from unilluminated sample.

Final [Pyrene] = concentration of pyrene extracted from illuminated sample

% Change = percent of photodecomposition of pyrene.

calculated utilizing Equation 12, p 28. Adsorbate concentrations are reported in micrograms of pyrene per gram of adsorbent. Uncertainties in the results in TABLE IV are expressed as 95% confidence intervals (number of measurements was four).

The iron oxides and four ferromagnetic ash fractions (Fe_3O_4 , Fe_2O_3 , VC68159 F1, KA F2, KA F3, and TX F3), as well as the nonferromagnetic fraction of Vince Conrad ash (VC68159 N1), stabilized adsorbed pyrene from photodecomposition, relative to pyrene adsorbed on glass, silica, alumina,^{6,7,15,16} and fly ashes that are low in iron and carbon content²⁶. From these data it can be inferred that fly ash particles with a significant amount of iron stabilize adsorbed PAH from photodecomposition.

Of the adsorbents examined in this work, only pyrene adsorbed on the ferromagnetic fraction of Vince Conrad ash # 67981 showed any significant photodecomposition. This may have been due in part to the large quantity ($\geq 358 \mu\text{g/g}$) of pyrene deposited on the surface. The FID was inoperative during the beginning of the deposition, so the amount of pyrene adsorbed by this particular ash fraction could not be determined. As stated earlier, it is assumed that pyrene would adsorb preferentially on the strongest adsorption sites first. After these sites were deposited, pyrene would then either be adsorbed on less retentive sites, or deposit on top of the pyrene already adsorbed (i.e., more than monolayer coverage). In either case, pyrene may be more likely to undergo photodecomposition than pyrene that is adsorbed on strong adsorption sites.¹⁴

The mechanism for how ferromagnetic fly ash particles stabilize adsorbed PAH from photodecomposition is not well understood. Korfmacher et al.⁷ suggested that transition metals may be able to quench a PAH molecule in the excited state and, thus, prevent it from undergoing photodegradation. Yokley et al.⁴ suggested that iron could be the primary mediator in this process. Behymer and Hites²³ suggested that the determining factor is not elemental composition as much as the color of the ash ("inner filter" effect). The mechanism by which iron appears to stabilize PAH from photodecomposition (on any fly ash substrate) remains to be elucidated.

B. Determination of the Power of a Xenon Lamp

Utilizing a Chemical Actinometer

1. The p-Nitroanisole/Pyridine Chemical Actinometer

A chemical actinometer solution of p-nitroanisole (PNA) and pyridine (PYR)³⁸, with a concentration of 5.48×10^{-4} M pyridine and 5.25×10^{-5} M p-nitroanisole, was utilized to determine the power and intensity of the xenon lamp used to illuminate PAH adsorbed on fly ash.

2. Data for Lamp Power Determinations Using the PNA/PYR Actinometer

The amount of photochemical product formed (n_b) was determined by analysis of the amount of reactant (n_a) remaining after irradiation, from the equation

$$n_a^0 - n_a^t = n_b, \quad (15)$$

where n_a^0 is the amount of reactant (number of molecules of PNA) before exposure to radiation and n_a^t is the amount of reactant remaining after being exposed to the radiation for time t . The amount of photochemical

product produced is dependent on the PNA concentration because PYR is the excess reactant (ratio of [PYR] to [PNA] is at least 10:1).

The quantum yield (Φ_p) of this reaction is dependent upon the pyridine concentration ([PYR], in M)³² and is determined from Equation 16 (p 44). The quantum yield for the actinometer solution in these determinations is determined for a pyridine concentration of 5.48×10^{-4} M. The quantum yield for the chemical actinometer utilized in this study was 5.21×10^{-4} . The average absorbance of the actinometer was determined to be 0.31 from Equation 14 (p 40) and Table I (p 42).

In the initial experiment ("Experiment I"), seven different solutions were illuminated for 1, 2, 5, 15, 30, 50, and 90 minutes, respectively. The lamp was turned on and off to start and stop the illumination. The power supply for the illumination lamp was set at 8 amperes. This experiment was performed in order to ascertain if the lamp was sufficiently intense to cause the actinometer to undergo a detectable photochemical reaction. This experiment was also performed to determine the optimum time of illumination. The data are summarized in Table V.

In "Experiment I", it was found that the apparent power of the illumination lamp decreased as the time of illumination increased. From these data, it was concluded that the optimum times of illumination were the shorter times (between 5 and 15 minutes). As the duration of illumination was increased, the absorbance of the actinometer underwent larger changes due to the change in the concentration of the photochemical reactants. The actinometry equation (Equation 7, p 12)

TABLE V

EXPERIMENT I

Determining the Optimum Illumination Time
Utilizing the PNA/PYR Actinometer

Irrad. time t, min	$n_a \times 10^{16}$	$n_b \times 10^{16}$	Power of Lamp photons/sec. $\times 10^{16}$
0	9.48	0.00	0.0
1	9.23	0.25	1.6
2	9.23	0.25	7.8
5	8.94	0.54	6.8
15	8.29	1.19	5.0
30	8.04	1.44	3.0
50	7.42	2.06	2.6
90	6.83	2.65	1.8

n_a - number of molecules of PNA remaining in solution.

n_b - number of moles of photochemical product produced.

3 ml of sample was illuminated.

Concentration of PNA prior to illumination was 5.25×10^{-5} M.

assumes that the absorbance of the actinometer remains constant throughout an experiment. Failure to adhere to these assumptions is expected to produce error, which can be minimized by using the shortest illumination time that produces a measurable concentration change. The minimum time of illumination was determined to be at least 5 minutes in order to cause a photochemical reaction (decrease in the concentration of PNA) that was readily detectable by HPLC.

Prior to "Experiments II and III", the lamp was allowed to warm up for thirty minutes. Actinometer solutions were then illuminated for 7, 10, and 13 minutes, respectively, using a power-supply current of 11 A. The lamp was left on continuously and a shutter was used to start and stop these illuminations. The data are listed in Table VI in the order in which they were obtained. These experiments were performed in order to obtain an estimate of the average power of the illumination lamp. "Experiments II and III" were performed on separate days.

The power of the illumination lamp appeared to fluctuate in both experiments. This was expected, as the lamp tends to "flicker" during an illumination. The average power (P_0^i) of the illumination lamp (with power supply set at 11 A) was found to be $(6.5 \pm 0.8) \times 10^{16}$ photons per second based on the average of all measurements in "Experiments II and III" (uncertainty expressed as 95% confidence interval, for 18 replicate measurements). Based on the precision of these data, the PNA/PYR chemical actinometer appears to be a viable system for determining the power of the lamp used in this photochemical study.

TABLE VI

EXPERIMENTS II and III

Power of The Illumination Lamp Utilizing the
PNA/PYR Chemical Actinometer

Irrad. time t, min	$n_a \times 10^{16}$	$n_b \times 10^{16}$	Power of Lamp photons/sec. $\times 10^{16}$
<u>EXPERIMENT II</u>			
7	8.47	1.01	9.0
10	8.33	1.15	7.2
13	8.29	1.19	5.7
7	8.71	0.77	6.9
10	8.26	1.22	7.6
13	8.53	0.95	4.6
7	8.67	0.81	7.3
10	8.76	0.72	4.5
13	8.63	0.85	4.1
<u>EXPERIMENT III</u>			
7	8.46	1.02	9.1
10	8.13	1.35	8.5
13	8.40	1.08	5.2
7	8.67	0.81	7.3
10	8.61	0.87	5.4
13	8.19	1.29	6.2
7	8.64	0.84	7.5
10	8.91	0.57	3.6
13	8.15	1.33	6.4

$$P_o^1 = (6.5 \pm 0.8) \times 10^{16} \text{ photons/sec}$$

TABLE VII

EXPERIMENT IV

Power of The Illumination Lamp When the
Lamp Current was Adjusted

Irrad. time t, min	$n_a \times 10^{16}$	$n_b \times 10^{16}$	Power of Lamp photons/sec. $\times 10^{16}$
7	8.13	1.35	12.1
10	7.50	1.98	12.4
10	7.20	2.28	14.3
13	6.44	3.04	14.7

"Experiment IV" was performed to determine if the power of the illumination lamp could be controlled by adjusting the current of the power supply. The lamp was allowed to warm up for 30 minutes prior to the experiment. The current of the power supply was set at 20 A. The data for this experiment are contained in Table VII.

The data from Table VII, "Experiment IV", show that the power of the lamp increased significantly when the power supply current of the illumination lamp was increased from 11 A to 20 A.

Power may be converted to intensity by dividing by the surface area of the sample exposed to radiation (see Appendix). The intensity of the xenon lamp (current at 11 A) was found to be approximately 137 W/m^2 (surface area of sample exposed to radiation was 3 cm^2). The lamp used in this work was found to be more intense than the lamp used by Behymer and Hites,^{15,23} which had an intensity of 17 W/m^2 .

CHAPTER IV

CONCLUSION

A. Fly Ash Research

1. Iron Content of Ferromagnetic Ash Fractions

The amount of iron present in ferromagnetic fractions of fly ash was observed to vary with the particular fly ash. Constituents (other than iron) that are present in the bulk ash are also present in the ferromagnetic ash fractions (e.g., carbon and silicon). From these observations it may be concluded that ferromagnetic fractions of ash are not pure iron oxides.

Iron was also determined to be present in nonferromagnetic ash fractions, but in lesser amounts than in ferromagnetic ash fractions. From these observations, it may be concluded that a magnet cannot be utilized to remove all of the iron from a size-fractionated fly ash. A magnet can be utilized to collect ferromagnetic fractions of ash that are enriched in iron relative to the iron content of nonferromagnetic ash fractions.

2. Observed Stabilization of Pyrene Adsorbed on Substrates

Pyrene adsorbed on the surfaces of Fe_3O_4 and Fe_2O_3 was observed to undergo no detectable photodecomposition when exposed to illumination for 24 hours. From these observations, it may be concluded that Fe_3O_4 and Fe_2O_3 stabilize pyrene that is adsorbed on their surface with respect to photodecomposition.

Pyrene adsorbed on the surfaces of ferromagnetic fractions of fly ash was observed to undergo either no or moderate photodecomposition when irradiated for 24 hours. The ferromagnetic fractions of fly ash (KA F2, KA F3, TX F3) that contained the greatest amount of iron (and the smallest amount of carbon) were observed to suppress, almost completely, the photodecomposition of pyrene adsorbed on their surfaces. The ferromagnetic fraction of "Vince Conrad" # 68159 (VC68159 F1) was also observed to stabilize the photodecomposition of surface adsorbed pyrene. Pyrene adsorbed on the surface of the ferromagnetic fraction of "Vince Conrad" ash # 67981 (VC67981 F1) was observed to undergo moderate photodecomposition when irradiated. From these observations, it may be concluded that fly ash fractions which contain a large amount of iron, which is in the form of iron oxides^{27,29,30}, stabilize surface adsorbed pyrene to photodecomposition. The exact mechanism for this phenomenon is not presently known.

Fly ash particles in general seem to inhibit the photodecomposition of surface adsorbed PAH.^{4,5,7,15,20-25} From these observations, it may be concluded that PAH adsorbed on the surfaces of fly ash particles (especially those with large quantities of carbon and iron) would not photodecompose completely, in the presence of sunlight, during the atmospheric residence times of the particles. Thus, PAH may remain on the surfaces of ashes for long periods of time. If this is the case, then these particles may pose a health problem based on: the amount of PAH on the surface, the toxicity of the adsorbed PAH, the ability of the ash to stabilize photodecomposition of surface adsorbed PAH, and the residence times of these ashes in the atmosphere.

More research is needed in this area in order to obtain some idea as to the overall environmental importance of these atmospheric pollutants. Do other pollutants in the atmosphere react with PAH adsorbed on fly to form compounds that are more (or less) carcinogenic than the parent PAH? What is the concentration of PAH and other potentially toxic compounds on the surfaces of fly ash? Is the fly ash in itself a health hazard? Is there a feasible and economical way to solve the problem of these pollutants? These and other questions need to be answered in order to obtain some idea of the magnitude of environmental problems that may be caused by these pollutants.

B. Actinometry

A chemical actinometer solution of p-nitroanisole (5.25×10^{-5} M) and pyridine (5.48×10^{-4} M) was utilized to determine the power (in photons/second) and intensity of the lamp used for photochemical studies in this laboratory. Using this actinometer composition, the optimum illumination time was between 5 and 15 minutes for the particular lamp used in this work. Illumination times shorter than 5 minutes did not produce a sufficient decrease in the PNA concentration to be readily detectable by the method of analysis. Illumination times longer than 15 minutes may reduce the concentration of PNA in solution significantly. This may result in a larger change in the absorbance of the actinometer and thus make the power determinations inaccurate.

The power of the lamp was observed to vary during the course of an actinometry experiment. The average power of the illumination lamp (with the power supply current set at 11 A) was determined to be $(6.5 \pm$

$0.8) \times 10^{16}$ photons per second.

The intensity of the lamp was found to be approximately 137 W/m^2 with lamp current set at 11 A. The lamp used in this study was more intense than the lamp used by Behymer and Hites,^{15,23} which had an intensity of 17 W/m^2 .

The power of the illumination lamp may be controlled by adjusting the current of the lamp power supply. The power of the lamp was observed to increase when the lamp current was increased.

If the illumination times are controlled, it seems that the PNA/PYR chemical actinometer is a viable system for determining the power of polychromatic radiation produced by a xenon lamp.

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APPENDIX

APPENDIX

Calculating Power and Intensity of the Xenon

Illumination Lamp

A. Determine Average Absorbance of Actinometer Solution

- (1) The absorbance of the actinometer solution at each 10 nm interval is determined from the absorption spectrum from 410-220 nm (e.g., 410 nm, 400 nm, 390 nm, ... 220 nm).
- (2) The output (W/nm) of the illumination lamp at each 10 nm interval (410-220 nm) is determined from the emission spectrum supplied by the manufacturer.
- (3) Convert output (P_i) of the lamp at each 10-nm interval to relative output (P_k), normalized to wavelength of 320 nm (in which the output of the lamp is at a maximum). This is accomplished by converting output from units of W/nm to W (multiply output (P_i) by wavelength (λ_i)) and dividing by the maximum output (0.52 W/nm at 320 nm). For example, the relative output (P_k) of the lamp at the intervals of 220, 320, and 390 nm, with outputs of 0.13, 0.52, and 0.47 W/nm, respectively, is calculated in the following manner.

$$(\lambda_i \times P_i) / (320 \text{ nm} \times 0.52 \text{ W/nm}) = P_k$$

$$(220 \text{ nm} \times 0.13 \text{ W/nm}) / (320 \text{ nm} \times 0.52 \text{ W/nm}) = 0.17$$

$$(320 \text{ nm} \times 0.52 \text{ W/nm}) / (320 \text{ nm} \times 0.52 \text{ W/nm}) = 1.00$$

$$(390 \text{ nm} \times 0.47 \text{ W/nm}) / (320 \text{ nm} \times 0.52 \text{ W/nm}) = 0.90$$

- (4) The average absorbance of the actinometer solution (A_a) is calculated from the following equation:

$$A_a = (\sum P_k A_k) / N$$

where N is the total number of intervals ($N = 20$), and A_k is the absorbance at wavelength λ .

B. Calculating Power of the Illumination Lamp

- (1) Determine quantum yield (Φ_b) of the actinometer solution.

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

- (2) Calculate power (P_o^i) from known values of illumination time (t , in sec), quantum yield (Φ_b), number of molecules of photochemical product produced (n_b), and average absorbance of the actinometer solution (A_a). The units are in photons per second.

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

C. Calculating Intensity of the Illumination Lamp

- (1) Convert power units from photons/sec to einsteins/sec.

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

- (2) Convert power units from einsteins/sec to kcal/sec (Energy is 90 kcal/einsteins at 320 nm).

$$(P_o^i, \text{ in einsteins/sec}) \times (90 \text{ kcal/einstein}) = (\text{kcal/sec})$$

- (3) Convert power (P_o^i , kcal/sec) to intensity (I_o^i , kcal/sec cm^2) by dividing power of the lamp by the surface area of sample (in cm^2) that is exposed to radiation.

- (4) Convert intensity to units of W/cm^2 using conversion factors.

$$(I_o^i, \text{ in kcal/sec-cm}^2) \times (1 \text{ kW-sec} / 0.239 \text{ kcal}) \times (1000 \text{ W/kW}) = (I_o^i, \text{ in W/cm}^2)$$

VITA

Anthony Dewayne Hipps was born in Florence, Alabama, on December 31, 1961. He graduated from Central High School in May, 1980. After graduating high school, he attended Freed-Hardeman College in Henderson, Tennessee and earned a B.S. in chemistry in May 1985. In September, 1985, he entered graduate school at the University of Tennessee, Knoxville. His interest outside of chemistry include softball, basketball, fishing, and other forms of outdoor recreation. Anthony is an active member of the Church of Christ and has served as a minister and youth director. He has also served as a coach for the special olympics.

One of Anthony's main philosophies is that everyone, regardless of race, sex, education, creed, intelligence, economic background, or occupation, should be treated with honor and respect. Every person is a special and unique creation.