

## ABSTRACT

Elizabeth Ann Hayes. A Method for Studying Heterogeneous Photochemical Reactions of Polycyclic Aromatic Hydrocarbons on Atmospheric Combustion Aerosols. (Under the Direction of Professor RICHARD KAMENS and Dr. STEVE McDOW)

Combustion aerosols are an important source of toxic atmospheric compounds, a major class of which is polycyclic aromatic hydrocarbons (PAHs). Photodegradation is an important atmospheric loss mechanism for PAHs. Combustion aerosols consist of an elemental carbon core and an organic layer. Several recent studies show that aerosol surface characteristics influence PAH photodegradation rates. Recent research indicates that organic layer constituents also strongly influence PAH photodegradation in organic liquids. These results prompted an investigation of the relative importance of aerosol surface characteristics versus composition of the organic layer.

Organic compounds found on combustion aerosols were incorporated on carbon black particles to simulate a heterogeneous aerosol environment. Organic compounds identified in diesel soot, and wood soot combustion aerosols were investigated to determine their influence on PAH reactivity. Solutions containing dissolved PAHs, and the organic compounds were syringe spiked on to a carbon black surface. A liquid dispersion technique for obtaining thin, even coatings of the organic particulate matrix on Teflon filters was used to facilitate UV light exposure to the synthesized particle matrices. The filter supported aerosol matrices were exposed to UV light in a photochemical turntable reactor.

The photodegradation rate of polycyclic aromatic hydrocarbons is significantly enhanced when isoeugenol, a compound found on wood combustion aerosols, is present with the PAH in the organic layer on elemental carbon particles. These results indicate that constituents which coexist with PAH in the organic layer around the elemental core influence the reactivity of PAHs on combustion aerosols. Further evaluation of specific chemical and physical properties of the organic layer and the elemental surface using the developed technique will lead to better characterization of PAH reactivity on combustion aerosol surfaces.

Organic compounds found on combustion particles are a major source of atmospheric pollutants which adversely affect human health. This investigation of physical and chemical factors influencing reactivity contributes to the knowledge about the stability, transport, and bioavailability of toxic compounds on combustion particles in the atmosphere.

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## 1. Introduction

The 1990 Clean Air Act Amendments addressed air pollution problems not solved by previous amendments to the 1970 Clean Air Act. A major concern of Congress has been the failure of the EPA to control emissions of air toxics, which are pollutants of known toxicity to human health. Listed among the air toxics are polycyclic organic matter (POM). A significant portion of the mutagenicity of organic extracts of POM may be attributed to polycyclic aromatic hydrocarbons (PAHs) and their transformation products (Nielsen et al., 1983). PAH are of significant concern due to their known animal carcinogenicity and widespread abundance in the environment (Valerio et al., 1984).

The main source of POM in the atmosphere is combustion of fossil fuels, including stationary sources such as coal burning plants, and mobile sources such as automobiles (Suess, 1976). Particulate matter emitted to the atmosphere during combustion typically contains an elemental carbon core coated by an organic layer. Combustion particles from different sources vary in chemical and physical properties. Diesel soot is largely elemental carbon with a thin organic coating which is predominantly non-polar (Japar et al., 1984; Schuetzle et al., 1981; Ross and Risby, 1982). Wood smoke is composed almost entirely of polar organic material such as methoxyphenols (Kamens et al., 1985; Hawthorne et al., 1989). PAHs represent from .5 to 5 % of the organic fraction of combustion aerosols (Ross et al. 1982, Kamens et al., 1988). The mutagenicity of combustion aerosols can be modified by the photochemical reactions of PAHs on the particle surface.

PAH distribution between the air and particle phases is proportional to vapor pressure, with higher molecular weight PAH found on the particle phase. The deposition properties of vapors and particles differ, thus the partitioning of PAHs between the two



phases will influence their transport in the lung and their atmospheric lifetime. PAH chemical reactivity will also be affected by the partitioning (Kamens et al., 1992). PAH present in the gas phase degrades by attack of OH radical. The half-life of PAH in the gas phase during smog episodes is short, from minutes to hours (Nielsen et al., 1983). Transformation rates of particle-associated PAH are influenced by physical and chemical properties of the particle. Particle-associated PAH reactivity is primarily due to photodegradation. (Atkinson, 1988). The photoreactivity of PAHs is not surprising, given their ability to absorb UV radiation above the atmospheric cutoff at 290 nm. The behavior of PAHs found in the gas and particle phase can be monitored using smog chamber studies. These studies permit conditions such as co-pollutant concentrations, and particle concentrations to be controlled. The photoreactivity of PAHs is evident in samples collected in a smog chamber located in Pittsboro, NC. PAHs present on combustion particles degrade in sunlight and are stable at night (Kamens et al., 1985, 1986, 1988).

Despite the known photodegradation pathways for PAHs in solution, photodegradation on combustion particles remains poorly understood. Particle surface characteristics seem to heavily influence PAH photodegradation (Behymer & Hites, 1985).

Another important determinant of PAH reactivity may be the associated organic compounds present in the extractable organic layer. Other constituents identified in wood combustion particles include methoxyphenols (Hawthorne et al., 1989). The presence of methoxyphenols enhances the photodegradation of PAHs in solution (McDow et al. 1991, 1992). The question remains, given the presence of methoxyphenols on soot particles, as to whether such photodegradation pathways occur in the atmosphere.

The goal of this research was to isolate the physical and chemical properties which influence PAH reactivity on combustion particles. A laboratory technique of exposing "model" particles to UV light in a turntable photoreactor allowed conditions to be controlled and simplified. Results of PAH reactivity when associated with organic

constituents on an elemental carbon surface will provide insight into the processes that occur on real combustion particles.

## 2. Background

Particle-associated toxic organic compounds, when deposited in the lung, may be released into the body causing possible adverse affects to human health. The causal relationship between air pollution and lung cancer deaths has been approximated as a 5% increase in the rate of lung cancer deaths for each increment of pollution as indexed by  $1\text{ng}/\text{m}^3$  of benzo(a)pyrene (BaP) in air. This relationship was endorsed by the National Academy of Science (Quraishi, 1985). BaP is a polycyclic aromatic hydrocarbon which has been shown to be carcinogenic in laboratory studies and linked to cancer in certain occupational studies (Greenberg et al., 1985).

In an attempt to protect human health, the EPA set national ambient air quality standards (1971) for total suspended particulate matter at  $260\text{ mg per m}^3$  for a 24 hour standard (Quraishi, 1985). Total suspended particulate (TSP) is that portion of ambient matter collected on a high volume filter for 24 hours with a cut size of  $30\mu\text{m}$ . In 1987, a revised national ambient air quality standard (NAAQS) for particulates was introduced which considered the respirable particulate fraction equal to or less than  $10\mu\text{m}$  - PM<sub>10</sub> (Hesketh, 1991). This was based on the knowledge that the fine fraction will penetrate into the lungs and potentially create a greater health risk than TSP (Hinds, 1982; Seinfeld, 1986). In addition there is evidence for the preferential concentration of toxic compounds on the smallest respirable particles (Natusch & Tompkins, 1978; Natusch, 1974, Fisher et al., 1979).

Principle sources of total suspended particulate matter include combustion of biogenic fuels, fossil fuels (coal, oil, gas, and gasoline), and incineration (Daisey et al., 1986). Important differences exist between the types of particles emitted from each



of these combustion processes. Analysis and characterization of ambient particulate matter on the basis of size, surface area, physical "porous" structure, phases present (solid, liquid), chemical composition of the liquid phase, and chemical characteristics of solid adsorption sites enhances our ability to evaluate the transport, fate, and potential health implications of emitted particulate matter from the various combustion sources.

The concentration of PAH in the atmosphere is determined by the emissions from combustion sources, and their atmospheric removal through physical and chemical mechanisms. PAHs are distributed between the gas and particle phases due to their intermediate vapor pressures (see Table 2.1). PAHs are distributed between the gas and particle phases because their vapor pressures are high enough to allow a significant gas phase component, but low enough that significant amounts are adsorbed on particulate matter. The atmospheric transformation processes of PAH depend on their distribution between the two phases (Atkinson, 1988, Bidleman et al., 1986, Schuetzle, 1975).

Table 2.1		
PAH Molecular Weight, PAH Vapor Pressure (torr) at 298K. (p.124 Atkinson, 1988)		
PAH	Molecular Weight (g/mole)	Vapor Pressure (torr)
Naphthalene	128	$8.0 \times 10^{-2}$
Anthracene	178	$6.0 \times 10^{-6}$
Fluoranthene (Fl)	202	$9.2 \times 10^{-6}$
Pyrene	202	$4.5 \times 10^{-6}$
Benz(a)anthracene (BaA)	228	$2.1 \times 10^{-7}$
Benzo(a)pyrene (BaP)	252	$5.6 \times 10^{-9}$
Chrysene	228	$6.4 \times 10^{-9}$

Gas phase mechanisms of OH radical attack on PAH, and other minor pathways are fairly well understood. Nitro-PAH products are formed from PAH when OH attack occurs in the presence of  $\text{NO}_x$  (Atkinson, 1988). Photo-induced processes of particle-associated PAH are thought to be the major mechanism responsible for PAH degradation (Kamens et al., 1988). Studies of PAH on particle surfaces show that the rate of PAH photolysis is strongly dependent on the surface characteristics (Behymer and Hites, 1985).

Photolysis during transport of PAH on combustion particles can lead to a loss of carcinogenic species (Nielsen, 1988) or an increase in mutagenic species concentration (Finlayson-Pitts and Pitts, 1986). There is disagreement concerning PAH particle phase reactivity in atmospheric systems (Behymer and Hites, 1988). Combustion particles differ in chemical and physical properties, therefore attempts to characterize PAH on all of them as being either stable or reactive may be misleading. Additionally, careful interpretation of PAH reactivity from ambient sampling data requires quantification of all factors which influence particle-associated PAH transformations as a function of sampling time (i.e. PAH concentration depends on ambient particle concentration). The seasonal variation of ambient particle associated PAH concentrations suggest that either additional combustion particles are present in the atmosphere in the winter, or that PAHs decay much faster in the summer (Pistikopoulos and Mouvier, 1990; Pierce and Katz, 1975; Sawicki et al., 1960). Studies which characterized both the total suspended particulate matter and extractable organic matter concentrations found that the increase in PAHs and extractable organic matter could not be accounted for due to an increase in particulate matter (Lioy, 1983; Sawicki et al., 1960). Additionally quinones, known products of PAH photodegradation, have also been found to vary with season, being highest in the summer and lowest in the winter (Pierce and Katz, 1976).

Rapid reactions of PAHs on combustion particles have been observed in smog chamber experiments. Sunlight is the primary determinant, with relative humidity, temperature, particle PAH loading, and combustion source (diesel, wood) also influencing the photodegradation rate (Kamens et al., 1988). PAH stability on stack collected fly ash samples exposed to ultraviolet radiation suggests that surface characteristics of this type of combustion particle stabilizes PAH reactivity relative to other particle types (Fisher, 1983; Raabe 1979). Other determinants of PAH degradation rates on combustion aerosols are being sought to help characterize the fate and transport of these compounds.

A method needs to be developed for evaluating PAH reactivity on heterogeneous combustion aerosol particles as a function of specific physical and chemical properties which are representative of the character of the PAH environment. Model irradiation conditions and model combustion aerosol generation systems have been employed to reduce the complexity inherent in an atmospheric combustion aerosol environment. The ability to infer PAH reactivity from model studies to real ambient organic particles is critically dependent on how well the physical and chemical properties of combustion particles are characterized and represented in the model systems. A systematic evaluation of the literature on ambient aerosol particles and characterization of combustion particles from different anthropogenic sources is given below.

Analysis of size fractionated ambient aerosols collected next to a heavily traveled highway indicate that the fraction less than 1  $\mu\text{m}$  consists of soot or carbonaceous material, and that PAHs are concentrated in this size fraction (Butler and Crossley, 1981). The 1-2 $\mu\text{m}$  size fraction consists also of carbonaceous material but is devoid of PAH, suggesting that this material was produced at higher combustion temperature. Presence of high concentrations of iron and sulfur in this fraction are characteristic of fly ash (Butler and Crossley 1981). Distributions of BaP with particle

size found in ambient air samples were reported by Miguel and Friedlander (1978). The BaP concentrations expected on each size fraction of particles generated during dark chamber wood smoke experiments are listed in Table 2.2 (Kamens et al. 1986). The measured particle size distribution in the chamber was fairly stable and did not cause a change in the measured PAH concentration (Kamens et al., 1986).

Table 2.2 %BaP Expected in Each Particle Size Range (Kamens et al., 1986)	
Particle size range ( $\mu\text{m}$ )	% of total BaP in each size range
.056 - .1	19
.1 - .178	49
.178 - .316	13
.316 - .562	11
.560 - 1	8

Combustion particles have been evaluated in terms of their percentage of elemental carbon to organic carbon content and this ratio was found to be highly source dependent, as listed in Table 2.3 (Finlayson-Pitts and Pitts, 1986). The variation among various sources of BaP has also been listed in Table 2.4 as compiled from Daisey et al. (1986), and Li and Kamens (1992).

Table 2.3	
Percentage Elemental to Organic Content for Combustion Particles	
(Finlayson-Pitts & Pitts, 1986)	
Combustion Source	Elemental Carbon/Organic Carbon
Coal furnaces	33%-95%
Automobiles, Diesel	75%-79%
Automobiles, Gasoline	26%-54%
Fireplace, Hardwood	32%
Fireplace, Softwood	1%

Table 2.4		
Concentrations of Benzo(a)pyrene in Particulate Matter from Various Sources		
Source	$\mu\text{g/g}$ BaP in particulate matter	Reference
Tunnel samples	66-500	Daisey, 1986
Coal Burning - Residential Anthracite	10-20	"
Coal Burning - Residential Bituminous	240-600	"
Coal Burning - Power Plants	$7 \times 10^{-4}$	"
Oil - Burning Power plants	.005	"
Residential wood burning - Fireplaces	3-141	"
Wood Stoves	213-870	"
Coke Plant	1400-5800	"
Soil	.1-2.3	"
automobile, diesel	81	Li, 1992
automobile, gasoline	189	"



The organic composition of combustion particles may also vary widely as a function of combustion source. Automobile gasoline engine exhaust particulates were characterized as consisting of 50% saturated aliphatic, 5% PAH, and 30% oxygenated hydrocarbons (Boyer and Laitinen, 1975). Allegheny tunnel samples consisted of 50% aliphatics, 10% PAH, and 21% very polar compounds (Salmeen et al., 1985). Analysis by fractionation of wood soot indicates that only 11-14% of the extractable organics were eluted in the neutral or semipolar fractions, probably aliphatic and PAHs, and 81-84% elutes in the most polar fraction, suggesting that most of the particle-bound organics in wood smoke are very polar in nature (Kamens et al., 1985). Specific extractable organic compounds have been identified on combustion particles, primarily in an attempt to identify compounds unique to particular sources for use as tracers. Aliphatics, aza-arenes (heterocyclic nitrogen compounds), PAHs, nitro-PAH, aliphatic and aromatic carboxylic acids, dicarboxylic acids, aromatic acids, ketones, quinones, phenols, and halogenated halocarbons are compound classes which have been characterized in filter collected ambient air particles, although knowledge about relative source contributions is incomplete. Polar organic compounds have been difficult to identify using current gas chromatography (GC) or liquid chromatography (LC) techniques due to their thermal instability, or reactivity with the column support. However, a number of methoxyphenolic compounds similar to lignin structural units have been identified in unfractionated wood combustion particle extracts (Hawthorne et al., 1989).

Polycyclic aromatic hydrocarbons absorb strongly in the ultraviolet radiation region and are readily photooxidized by ultraviolet light transmitted through the atmosphere. The rate of photoreactivity increases with increasing polarity of the solvent when PAH's are irradiated in liquids (Nielsen et al., 1983). PAH half-lives in toluene are found to be directly reduced when methoxyphenols are added to the solution, and photodegradation of PAH in pure methoxyphenols is 10-30 times faster

than in pure hexadecane (McDow et al., 1991). The relative importance of surface characteristics and organic layer composition in determining PAH reactivity on combustion particles remains to be determined.

Results of PAH reactivity experiments using model combustion particles are often difficult to interpret due to the different protocols used. Variations in the ultraviolet source, particle surface area, PAH concentration, and particle surface properties must all be characterized prior to determining their intercomparability and relevance to real combustion particles (Valerio et al., 1984). Table 2.5 concisely describes the protocol and results for PAH reactivity measurements on model combustion surfaces from several investigators.

Table 2.5

## Review of Heterogeneous PAH Photodegradation Experiments

Investigator	Reactor	Irradiation Source	Substrate	Surface Area ( $\text{m}^2/\text{g}$ )	PAH concentration $\mu\text{g/g}$	PAH coverage $\mu\text{g}/\text{m}^2$	Half-Life of PAH (hrs)
Behymer & Hites (1985)	rotary cell	Mercury lamp, 17.6W/m <sup>2</sup>	Silica gel	637	450 $\mu\text{g/g}$ of mixed PAH	.706	4.7
Behymer & Hites (1985)	*	*	alumina	224	450 *	2.0	1.4
Behymer & Hites (1985)	*	*	fly ash	5.1	450 *	88	31
Behymer & Hites (1985)	*	*	carbon black	11.6	450 *	39	570
Thomas & Tebbins (1968)	tubular cell 11ftx6in	*	acetylene soot	unknown	1800 $\mu\text{g/g}$ , BAP		< 1 (58% loss 40min)
Daisey et al., (1982)	fluidized bed	200W Hg vapor lamp, 36W/m <sup>2</sup>	coal fly ash	2 - 9	570 $\mu\text{g/g}$ , Pyrene	63	7
Korfmacher et al. (1980)	rotary cell	150W Xenon Arc Lamp	coal fly ash	7	75 $\mu\text{g/g}$ BaP	10.1	> 76
Daisey et al. (1982)	fluidized bed	200W Hg Vapor lamp, 36W/m <sup>2</sup>	carbon black, carbosieve S	860	80	.093	> 23
Kamens et al. (1985)	Smog Chamber	Sunlight, .2- .3cal/cm <sup>2</sup> /min	carbon black, aerosolized	230	100	.44	> 10
Fox & Olive (1979)	filters	Sunlight	enriched atm. part.	unknown	unknown	unknown	short

The influence of physical and chemical characteristics of combustion particles on the photo-reactivity of adsorbed PAH must be identified to accurately assess reaction mechanisms. PAH concentration on the particle surface is an example of one factor which influences the photodegradation rate, which might explain discrepancies which exist among reported half-lives of PAHs when the particle substrate is identical. Fly ash had been investigated as a surface which stabilizes PAHs. However, investigators have reported different reactivities for PAH on fly ash. Korfmacher et al. (1980a, 1980b) found that only 11% of BaP degraded upon exposure to 190 hours of radiation. Photodecomposition initially occurred rapidly but stopped after only a small fraction of BaP degraded. Daisey et al. (1982) found that pyrene adsorbed on fly ash degraded much faster when exposed to light, and had a half life of 7 hours. The systems employed to expose the particles to light are different but have been compared by Behymer and Hites (1988) and shown to give equivalent results. Korfmacher employed a rotary reactor where particles are rotated in a cell which is transversely irradiated by a light source (1980b). A fluidized bed photoreactor was designed by Daisey et al. (1982) to enhance light exposure to particles by suspending them in a gas flow. The PAH concentrations adsorbed on the fly ash varied between  $63\mu\text{g/g}$  in Korfmacher's study and  $570\mu\text{g/g}$  in Daisey's study. Although different PAH were used in these studies, similar reactivity is expected for pyrene and BaP. The differences in the two studies is not likely to be due to differences in specific compounds. The vapor deposition technique used by Korfmacher allowed monolayer adsorption of PAHs from the vapor phase, to mimic the condensation processes undergone by PAHs in the stack of coal furnaces (1980b). In Daisey's experiment, the PAHs were adsorbed onto fly ash using a slurry coating technique, where the concentration adsorbed is determined by varying the solution concentration applied. Different types of fly ash may also account for the difference in rates observed (Behymer and Hites, 1988). These examples

illustrate the importance of knowing what factors to control in experiments of PAH photodegradation on model and real particles.

Adsorption of PAHs on fly ash has been studied by Eiceman and Vandiver (1983), using elution analysis, showing that the adsorption isotherms are irreversible at concentrations below  $30\mu\text{g/g}$  concentration of PAH. Therefore, PAHs which are chemisorbed or adsorbed in an irreversible manner to the surface of fly ash may not be able to undergo photodecomposition. This could explain the discrepancy between results of Daisey et al. (1982) and Korfmacher et al. (1980a). PAHs adsorbed on top of previously sorbed PAHs or other organics would be able to undergo photochemical reactions as is observed in solution. The concentrations of extractable organics found on fly ash sampled from industrial stacks suggests that PAHs on fly ash in the atmosphere are present as less than a monolayer. If the particle substrate and PAH concentration are the controlling factors in the atmospheric system, then Korfmacher's results of stability may be atmospherically relevant for fly ash particles emitted from industrial stacks.

Considerable care must therefore be taken when designing a system to model particle associated organic compounds. The emphasis of this research was to model a heterogeneous two phase solid-liquid combustion particle so as to evaluate the important physical and chemical factors of combustion particles which determine PAH photoreactivity. The model combustion particle contained PAHs dissolved in an organic layer surrounding a carbon core. The criteria for a model system was that particles be consistently generated, that the organic composition could be easily modified, and that the particles be readily accessible to exposure to ultraviolet radiation. In the method developed, selected organics were coated onto carbon black particles along with the PAHs.

The goal of this study was to develop a technique to model, in an atmospherically relevant manner, the PAH photodegradation on combustion particles.



Distribution of a PAH in the environment depends on whether the PAH has a stronger affinity for the solid, liquid or gas phase, as is influenced by its vapor pressure, solubility, and adsorptive properties. The photoreactivity of a PAH varies depending on whether it is in a vapor, solution, or solid phase. PAHs primarily on the particle phase are in close proximity to other organic compounds also adsorbed on the particle surface. This investigation of the particle associated PAH reactivity addresses the role of associated organic compounds in addition to the role of elemental carbon surface characteristics.

### 3. Procedure

A method was developed using a liquid phase technique to prepare uniform multicomponent organic coatings on carbon black particles, and to uniformly distribute the coated particles on supportive Teflon filters. This method permits the adjustment of the composition and amount of constituents in the organic coating, and the type of surfaces used, so that realistic PAH environments on combustion particles can be generated and studied. Particles were exposed to ultraviolet light and subsequently analyzed for evidence of PAH photodegradation over time.

Figure 3.1 illustrates the methodology and apparatus used in this study. Multicomponent organic coated carbon black particles were dispersed on Teflon filters. After coating and dispersing the multicomponent particles onto duplicate filters, the samples were supported on a turntable which encircled a water-cooled UV lamp. Samples were removed from the turntable reactor at different intervals during the exposure period. The samples were then extracted using a mini-Soxhlet extraction apparatus and prepared for analysis by reverse phase HPLC and GCMS. Determination of the rate of photochemical transformation of PAHs was determined from analysis of the filter samples.

#### 3.A Buchner Funnel Liquid Particle Coating and Dispersion Technique

The coating technique required specification of five components: 1) Target Compound for Photoreactivity analysis, 2) Co-reacting Organic Species, 3) Particle Surface, 4) Dispersion liquid, and 5) Filter. The selection of representative PAHs was based on their ability to absorb atmospheric UV (see Figures 3.2 and 3.3) and on

the existing data base on liquid phase reactivity. The PAH spectra were obtained from Finlayson-Pitts and Pitts (1986). The isoeugenol spectrum was obtained with a HP 8451A Diode Array Spectrophotometer (UV-VIS). The absorption spectrum in Figure 3.2 plots the amount of light adsorbed by a compound, or  $\log e$ , the log of the molar extinction coefficient as a function of wavelength. The molar extinction coefficient of a compound reflects its ability to absorb light and may be defined using the Beer-Lambert absorption law (equation 3.1).

$$I/I_0 = 10^{-\epsilon c l} \quad \text{eq. 3.1}$$

$I_0$  = incident light,  $I$  = transmitted light,  $\epsilon(\text{l/mol}\cdot\text{cm})$  = molar extinction coefficient,  $c$  = concentration of absorbing species,  $l$  = path length.

The concentrations chosen were in the same range as those found on combustion-generated particles collected from the atmosphere. A number of PAHs were chosen so that possible effects of differing vapor pressures or solubility on reactivity within the matrices could be monitored. Constituents of the organic layer were chosen which exhibited strong influences on PAH photodegradation in liquid phase experiments (see Figure 3.4). Concentrations of these co-reactive constituents were chosen to be similar to concentrations observed on combustion particles (Hawthorne et al., 1989). A model combustion surface which had surface areas, surface functional groups and carbon content similar to atmospheric combustion particles was chosen. Criteria for surfaces were that they be well characterized in addition to being similar to combustion-generated particle surfaces, such as is the case for carbon blacks. The dispersion solvent was to be easily evaporated from the particles and the filter. Solvents and filters were selected which maximized the amount of PAH adsorbed on the particles and minimized adsorption on the filters. Coating components were to be miscible with the dispersion liquid yet the dispersion liquid was not to compete with the PAH, isoeugenol or other coating components for adsorption to the surface of the carbon black. The supportive filter upon which the particulate matter

was evenly dispersed was to be nonadsorptive to all of the constituents, so that the coating remained attached to the particle surface rather than to the filter surface.

The following procedure was used to obtain an evenly-distributed, thin layer of coated particle on Teflon filters. 1 mg Carbon Black (Development Carbon T10121 [Citco]) was syringe-spiked with 400 $\mu$ l of the multicomponent coating dissolved in dichloromethane. The mixture was sonicated for one minute in a 2ml glass vial, then the dichloromethane was evaporated, leaving the coating on the particles. The coated particles were then deposited on a 2 $\mu$ m pore size, 47mm Zefluor filter. Zefluor filters are a tortuous path filter Teflon membrane with a chemically resistant Teflon backing. The particles were evenly dispersed on the filter using a Büchner funnel. 25ml of dichloromethane solvent was placed in the Büchner funnel over the Zefluor filter. The coated particles were scraped out of the glass vial using a spatula and washed with dichloromethane into the Büchner funnel. Particles which could not be retrieved off the glass vial with a spatula were sonicated briefly, as extensive sonication would extract the coating from the particles (Daisey et al., 1986). Once all the particles were suspended and dispersed in the liquid above the Büchner funnel a vacuum was applied, drawing the solvent through the filter, and leaving the particle/coating matrix distributed evenly on the filter.

The Büchner Funnel Filtration Technique: The Büchner funnel filtration (BFF) technique first involved coating carbon black particles in a small vial and then transferring the particles to the Büchner funnel. A variety of transfer techniques were evaluated. First, the coated particles were resuspended in a small volume of solvent. Then the coated carbon black particles were scraped off the walls of the glass vial using a spatula (spatula method) or removed from the walls using sonication (sonication method), then transferred to the filter. The reference method for complete transfer of coated particles to the liquid phase was to use glass wool to collect the particles and

clean the walls which then were placed in a thimble for extraction. This method was only used as a test for performance of the spatula and sonication methods.

An alternative method of adsorbing the compounds from a liquid phase onto the carbon black particles was investigated. Carbon black and the organic constituents were separately placed in the Büchner funnel, so the step of transferring coated particles from a vial to the liquid phase could be eliminated (no transfer method). Adsorption of the organic constituents from solution to the carbon black surface would be controlled by their diffusion rates in solution, the number of collisions with the surface, and the adsorption strength.

The Slurry Coating Technique: Other coating techniques were attempted before and during development of the Büchner funnel filtration (BFF) technique. Initial experiments measuring PAH reactivity on filter surfaces in the dark and exposed to light were performed with the PAH slurry coated on the filters. To initially determine the effect of carbon black on PAH reactivity in the light and dark, PAHs were slurry coated on bare filters and filters containing carbon black. Using this method a slurry coating of carbon black, PAH, organics and dichloromethane are deposited on to a filter. The dichloromethane is allowed to evaporate. PAH and organics remain coated on to the carbon black on the filter. An initial experiment was performed to measure the influence of isoeugenol on PAH reactivity on particles. For this experiment, two slurry coatings were prepared in dichloromethane, one containing isoeugenol and PAH and one containing PAH for application to carbon black particles on filters.

### 3.B Turntable Photoreactor

After coated particles were deposited on filters, the filters were then placed in a Turn-table photoreactor illustrated in Figure 3.1. The turntable arrangement permitted all of the filters to be exposed to the same amount of light, as they all rotated around a



cylindrical lamp, minimizing any positional dependence in the exposure process. Use of a stable, consistent light source and specific exposure configuration helped reduce the variability in exposing these samples to light. The turntable was modified by making Teflon filter holders to occupy standard test-tube positions, to support 9 filters of 47 mm size. During the process of being rotated around the lamp the filters were vertical, therefore the method was sensitive to the particles' ability to remain on the filter during the exposure process. A 450 Watt high pressure quartz mercury vapor lamp was used to generate the UV radiation to which the samples were exposed. The spectral distribution of the lamp consisted of discrete emission lines in the UV region; Figure 3.3 illustrates the spectral distributions of the Hg lamp and the sun. The Mercury UV lamp was placed in either a quartz or a borosilicate water cooled immersion well. The emission wavelengths to which the samples were exposed was specified by choice of the immersion well and light filters placed around the lamp. The immersion well was cooled using a Little Giant Model 1-AA submersible pump (Little Giant Pump Co., Oklahoma City, OK), which cycled distilled deionized well water through the immersion well and an ice bath at 1 liter/min. The stability of the ultraviolet light intensity generated by the lamp was continuously monitored with an Eppley Ultra-Violet Radiometer (Eppley Laboratory, Inc., Newport, R.I.)

### 3.C Soxhlet Extraction

Before the samples were extracted, an internal standard of 5 $\mu$ l or 10 $\mu$ l of 100ng/ $\mu$ l of b-b'-binaphthyl was added to the extraction flask along with 30 ml of dichloromethane. Filters were individually extracted using micro-soxhlet extractors for 12 hours. Dichloromethane was reduced to a volume of 1 ml using a Kuderna-Danish column, and the entire sample was transferred to a tared vial. Next the sample was blown down to almost dryness to exchange dichloromethane with acetonitrile, and to place the constituents in a known volume of acetonitrile (typically 100 - 400  $\mu$ l).

Dichloromethane was chosen over toluene to extract the organic constituents from the carbon black to avoid losses of compounds through volatilization during the solvent reduction steps (Daisey et al., 1986).

### 3.D HPLC

Analysis was performed using a Spectra Physics 8700 gradient elution HPLC, with a reverse phase column, ultraviolet excitation, and fluorescence detection. A manually packed precolumn was used to protect and prolong the lifetime of the analytical column. LiChroprep RP-18 (a hydrocarbon phase C16 chemically bonded to silica gel), particle size 25-48 $\mu$ m, catalog #9303 by EM Reagents was used to pack the precolumn. The analytical column (Supelcosil LC-PAH column with 5 mm packing, 15 cm x 4.6 mm, Supelco catalog number 5-8318M) was specifically designed for analysis of priority pollutants including PAH's. The mobile phase was water and acetonitrile of high purity grade, either Fisher Scientific's Optima or HPLC Grade. The SP 8700 HPLC was equipped with a helium degassing manifold. Degassing of the solvents was necessary to ensure that bubbles do not form on the low pressure side of the pump. The gradient elution solvent program for PAH analysis is listed in Table 3.1.

Table 3.1: HPLC GRADIENT ELUTION SOLVENT PROGRAM

Time (minutes)	%Water	%Acetonitrile
0	50	50
4	35	65
10	10	90
16	0	100
18	50	50
20	50	50

A Shimadzu Variable Wavelength Fluorescence Spectrophotometer (model 530) was used to detect fluorescent compounds including PAHs. The specificity of fluorescence detection eliminates much of the interference due to compounds which may coelute with the PAHs, and the sensitivity of this detection system is on the order of 1  $\mu\text{g/L}$ . Although the wavelength could be varied to identify specific PAHs by their absorbance and fluorescence characteristics, a fixed excitation and emission wavelength pair of  $\lambda_{\text{ex}} = 250\text{nm}$  and  $\lambda_{\text{em}} = 400\text{nm}$  was used to detect all of the PAHs. The main limitation of using the HPLC system was that many of the photochemical reaction products could not be identified, or were simply not detected if they did not fluoresce.

### 3.E Gas Chromatography/ Mass Spectrometry (GCMS)

Analysis of the extracted organic compounds was also conducted using a Hewlett-Packard GCMS, which could positively identify compounds by their mass spectra. A microliter of sample was injected onto either a split/splitless or cool on-column inlet of the HP5890A GC onto a DB-17 fused silica capillary column with .32mm or .25mm ID, .15 $\mu\text{m}$  film, and 30m length which was interfaced to the

HP5971A Mass Selective Detector (MSD). Helium was used as the carrier gas; the inlet temperature and oven temperature program varied depending on the injection inlet (split/splitless vs on-column, see Table 3.2a and 3.2b) and solvent used. MS Chemstation for DOS on a Hewlett Packard 386 personal computer was used to control the GC and MSD parameters during a run and for subsequent data analysis. When analyzing for products full scan ion chromatograms were obtained of the filter sample extractions, which were injected directly on-column to the GCMS.

Table 3.2a

Temperature Program for the GC Oven for On-column injection

Oven initial T: 100 °C, oven maximum T: 350 °C

Detector: 300 °C, Injector B(on col): 100 °C, Run time = 26.2 minutes

Rate (°C/min)	Oven Final Temp (°C)	Final Time (min)
15	250	0
5	280	10

Table 3.2b

Temperature Program for the GC Oven for Split-Splitless injection

Oven initial T: 100 °C, oven maximum T: 350 °C

Detector: 300 °C, Injector A(split-splitless): 300 °C, Run time = 30.3 minutes

Rate (°C/min)	Oven Final Temp (°C)	Final Time (min)
10	250	0
5	300	10

### 3.F NBS Standards

Work up and analysis methods were tested, optimized, and then verified using NBS Standards. The NBS Diesel Soot 1650 was used to test extraction efficiency and reproducibility. The NBS 1647b mixture of the PAHs in acetonitrile was used to quantify the peak areas obtained from the chromatograms to the known concentrations. Three standard samples, each serial dilutions of NBS 1647b were typically analyzed for each experiment to generate a calibration curve relating the integrated area data and concentrations.

### 3.G Calculation of Reaction Rates

A pseudo-first-order rate expression has been used to represent PAH decomposition on wood combustion particles exposed to solar radiation in a smog chamber (Kamens et al., 1985). In a first-order reaction the reactant concentration decreases exponentially with time. This behavior has been observed for the photodegradation of the PAH adsorbed on to the carbon black particles in many of the experiments performed. The first-order rate law for PAH disappearance may be expressed by equation 3.2a.

$$\frac{-d[\text{PAH}]}{dt} = k[\text{PAH}] ; [\text{PAH}] = [\text{PAH}]_0 \text{ at } t=0 \quad \text{eq. 3.2a}$$

where  $[\text{PAH}]$  is the concentration of PAH and  $k$  is the rate constant.

Equation 3.2a rearranges to equation 3.2b:

$$\frac{1}{[\text{PAH}]} d[\text{PAH}] = -k dt \quad \text{eq. 3.2b}$$

and when integrated yields equation 3.2c:

$$\ln \frac{[\text{PAH}]_t}{[\text{PAH}]_0} = -kt \quad \text{eq. 3.2c}$$



$[\text{PAH}]_0$  is the initial concentration of PAH,  $[\text{PAH}]_t$  is the concentration of PAH measured at time  $t$ . If  $\ln \frac{[\text{PAH}]_t}{[\text{PAH}]_0}$  is plotted against  $t$ , then a first order reaction will give a straight line. The rate constant  $k$  may be determined from the slope. A useful indication of the rate of a chemical reaction is the time it takes for the concentration of a substance to fall to half its value. This is the half-life, expressed as  $t_{1/2}$ , and may be calculated for a first order reaction using equation 3.2c. This is illustrated in equation 3.3a, which may be solved to give equation 3.3b

$$kt_{\frac{1}{2}} = \ln \frac{\frac{1}{2}[\text{A}_0]}{[\text{A}_0]} \quad \text{eq.3.3a}$$

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} \quad \text{eq.3.3b}$$

For a true first order reaction the half-life of a reactant will be independent of the initial concentration. The results obtained for PAH photodegradation due to photolysis were expressed in terms of the PAH half-lives by applying a linear least square regression for each plot of  $\ln \frac{[\text{PAH}]_t}{[\text{PAH}]_0}$  versus  $t$ . The square of the sample correlation coefficient  $r^2$  measures the strength of this linear relationship, but when no photodegradation occurs this measure is inadequate. This is also true for other cases when a straight line model is not appropriate.

### 3.H BET Surface Area

Characterization of the carbon black used to represent the combustion surface was also undertaken. Surface area analysis of the carbon black was performed by Micromeritics, of Norcross GA. The surface area of a particle may be determined based on the amount of an inert gas ( $\text{N}_2$ , He) of known size which is adsorbed by the

surface. The adsorption isotherm named after its authors, Brunauer, Emmett and Teller, can be used to calculate accurately the surface area from the plot of partial pressure of a gas versus isotherm parameters, and the surface area can be calculated from the slope and intercept (Castellan, 1983). The isotherm (equation 3.4a) assumes multilayer adsorption may occur at high pressures.

$$V/V_{\text{mon}} = cz / ((1-z)(1-(1-c)z)) \quad \text{eq. 3.4a}$$

V is volume of adsorbed material,  $V_{\text{mon}}$  is the volume adsorbed for complete monolayer coverage, c is a constant,  $z = p/p^*$ , p is the equilibrium vapor pressure,  $p^*$  is the bulk vapor pressure (temperature dependent). Equation 3.4a may be rewritten to obtain equation 3.4b.

$$1/(z-1)V = 1/cV_{\text{mon}} + (c-1)z/V_{\text{mon}} \quad \text{eq.3.4b}$$

A plot of  $1/(z-1)V$  versus z will permit evaluation of  $(c-1)/V_{\text{mon}}$  as the slope and  $cV_{\text{mon}}$  as the intercept, which combined will give c and  $V_{\text{mon}}$ . Once the volume of gas adsorbed on a monolayer is obtained, the number of  $\text{N}_2$  molecules in the monolayer on the surface may be calculated from the ideal gas law,  $n = PV/RT$  at  $T=273 \text{ K}$  and  $p = 1 \text{ atm}$ . From the number of nitrogen molecules on the surface, the surface area available for monolayer adsorption may be determined using a  $\text{N}_2$  molecular cross-section of .162 nm.

### 3.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy photographs of carbon black particles on Teflon filters were obtained. Characterization of the nature of the organic liquid phase and its

interaction with the surface was also attempted by taking SEM photographs of the filter supported carbon-organic layer matrices.

Scanning Electron Microscopy of particle surfaces generates an image which conveys more about the shape of particles, roughness, and roundness than optical microscopy. This is a result of the increased depth of field. The disadvantage of SEM is the necessity of examining the samples under vacuum, to generate a stable electron beam. The vacuum may cause volatile compounds which are present on particles to desorb from the particle surface, altering the particle characteristics during the process of analysis. The SEM is located in the electron microscopy laboratory in the Pathology Department of the UNC Medical School. Before placing samples in the SEM, the surface of the sample was made electrically conductive so that current from the electric beam would not build up on the particles. This was accomplished by coating samples with a thin conductive material. To coat the particles 2 mm x 2 mm snips of the filters, mounted on metal studs, were placed in a sputter coater chamber. The chamber was evacuated and argon was added to create an argon atmosphere. A tungsten filament heated and vaporized a thin gold-palladium wire. This placed a thin layer a few atoms thick on the sample and filter, which was not sufficient to affect the measurement of particles larger than  $.01\mu\text{m}$ .

The filter samples were loaded into the Scanning Electron Microscope when the electron beam was off. The SEM diffusion pump was turned off, and nitrogen gas was added to vent the electron microscope chamber. A transfer arm was opened, and samples on metal studs were placed on the stage along with a standard. The chamber was pumped down to a vacuum, and then the electron beam was turned on. The electron beam scanning speed, magnification, focus, contrast and brightness were adjusted using the standard. The stage was rotated manually to place each sample under the beam for examination.

Pictures of SEM images were obtained with a split image, where the right frame gave 8 to 10 times the resolution of a small rectangular region of interest specified within the frame on the left. The scanning electron microscopy pictures were used to determine the particle size distribution using a transparency of the Porton eyepiece graticule, which was then calibrated using the line rule displayed on the SEM photograph. The results were plotted on cumulative log-probability paper, a count median diameter was determined, and from this a mass median diameter by assuming uniform density.

Zefluor filters were used to support the particles during the SEM analysis. A more homogeneous filter with smaller pore sizes would have been preferable; however, it was difficult to acquire filter material resistant to degradation from the solvent which was used to disperse the particles on the filter (Nucleopore no longer manufactures filters whose membranes were made of Polyester with a pore size of  $.2\mu\text{m}$ ). The particles examined using Scanning Electron Microscopy were prepared in an identical fashion to the particles which were prepared for photodegradation experiments. Filters which contained particles coated with PAH and three different concentrations of isoeugenol were prepared using the Büchner funnel filtration technique for SEM analysis. A filter containing carbon black with no coating, and filters which had coating but no carbon black, were also prepared using the BFF technique for SEM analysis. SEM photographs of a blank filter were also obtained to determine the structure of the filter surface.

### 3.J Optical and Fluorescence Microscopy

Optical and Fluorescence Microscopy permitted the fluorescent organic compounds in the liquid layer to be observed on the particle surface, and permitted evaluation of the distribution of benz(a)anthracene and isoeugenol in the liquid layer surrounding the elemental carbon particles. A Leitz orthoplan 2 optical microscope

which was equipped with both a tungsten and a mercury lamp and an Orthomat E camera was used to generate photographic images of particles and the PAHs in the sorbed liquid layer. A 25X phase contrast objective lens was used to magnify the particles, and color film was used to capture the image of the green fluorescence emitted by the benz(a)anthracene present in the coating surrounding the particles when illuminated with the mercury lamp. Thin Teflon sheets were cut out to support particles which were coated with a variety of organics and mixtures of organics including benz(a)anthracene dissolved in dichloromethane, isoeugenol, and hexadecane. Filter samples were also prepared using the Büchner funnel filtration technique. Filters which supported carbon black particles coated with benz(a)anthracene only, and particles coated with both benz(a)anthracene and isoeugenol were prepared for analysis using the Optical/Fluorescence Microscope.

### 3.J Carbon black particle sizing using an Andreasen Sedimentation Pipet

Stoke's law describes the settling of particles in a quiescent fluid, and it may be applied to predict the particle size distribution of particles using either air or liquid fluids. If no mixing occurs in the fluid so that the system is in equilibrium, then the force of gravity may be equated with the resistant forces on the particles due to the fluid media as in equation 3.5a and 3.5b.

$$F_g = F_R \quad \text{eq. 3.5a}$$

$F_g$  is the force due to gravity,  $F_R$  is the resistant force of the fluid.

$$mg = 2p\mu_m u d \quad \text{eq.3.5b}$$

$m$  is particle mass,  $g$  is acceleration due to gravity;  $\mu_m$  is fluid viscosity;  $u$  is velocity,  $d$  is particle diameter. Equation 3.6 relates the mass of a particle to its diameter and the fluid and particle densities and when substituted into equation 3.5b for mass yields equation 3.7.

$$m = (\rho/6)d^3(\rho_p - \rho_m) \quad \text{eq. 3.6}$$



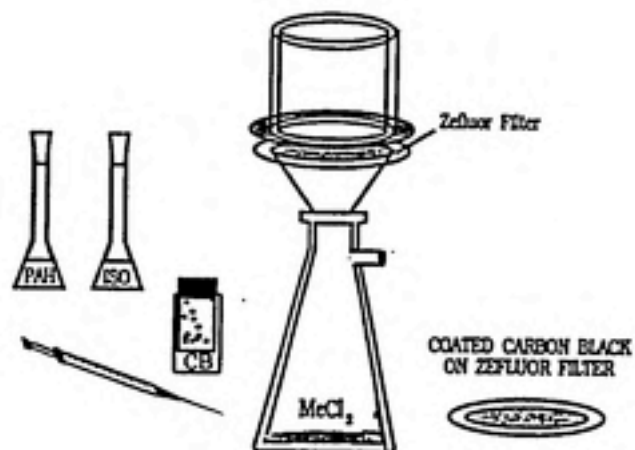
$m$  is the mass,  $d$  is the particle diameter,  $r_p$  is the particle density,  $r_m$  is the fluid or medium density. Equation 3.7 has been developed to determine the particle diameter as a function of settling velocity, or at specific times with measured settling distance.

$$d = 18m_m H / ((r_p - r_m)gt)^{1/2} \quad \text{eq 3.7}$$

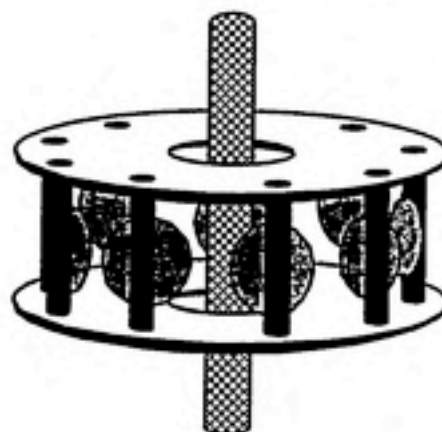
$d$  is particle diameter,  $m_m$  is fluid viscosity,  $H$  is distance particle has fallen in time  $t$ ,  $r_p$  is the particle density,  $r_m$  is the fluid density,  $g$  is the acceleration due to gravity,  $t$  is time.

A commercially available Andreasen Sedimentation Pipet (loaned to us by Dr. David Leith) was used to determine the particle size distribution of the organically coated particles generated by using the BFF technique. The Büchner funnel filtration technique is a liquid based technique, therefore a liquid based settling technique was preferred to determine the actual size of particles generated during particle preparation. The liquid used in the BFF technique to coat the particles was dichloromethane. The apparatus was placed in a hood, and the dichloromethane was allowed to equilibrate for several hours prior to use. Four grams of carbon black which were coated with isoeugenol were added to the pipet along with the dichloromethane; the apparatus was shaken vigorously for two minutes. Ten milliliter samples were then drawn from the bottom of the pipet into a tared aluminum weighing pan. The dichloromethane was allowed to evaporate at room temperature overnight, and then the final weights were obtained. Nine samples were taken every 2.5<sup>n</sup> minutes,  $n = 0$  to 9. This allowed the particles to be classified into nine size ranges between .6 $\mu$ m and 29.6 $\mu$ m. The total particle settling time was 2.6 days, during which time the pipet was immobilized to prevent disturbance of the dichloromethane. The temperature within the lab also remained fairly constant which helped to minimize the convective fluid motion.

### Buchner Funnel Filtration Apparatus



### Turn Table Photo-reactor



### Micro Soxhlet Extractor



Figure 3.1. Apparatus used to prepare, expose to light, and extract organic coated carbon black particles

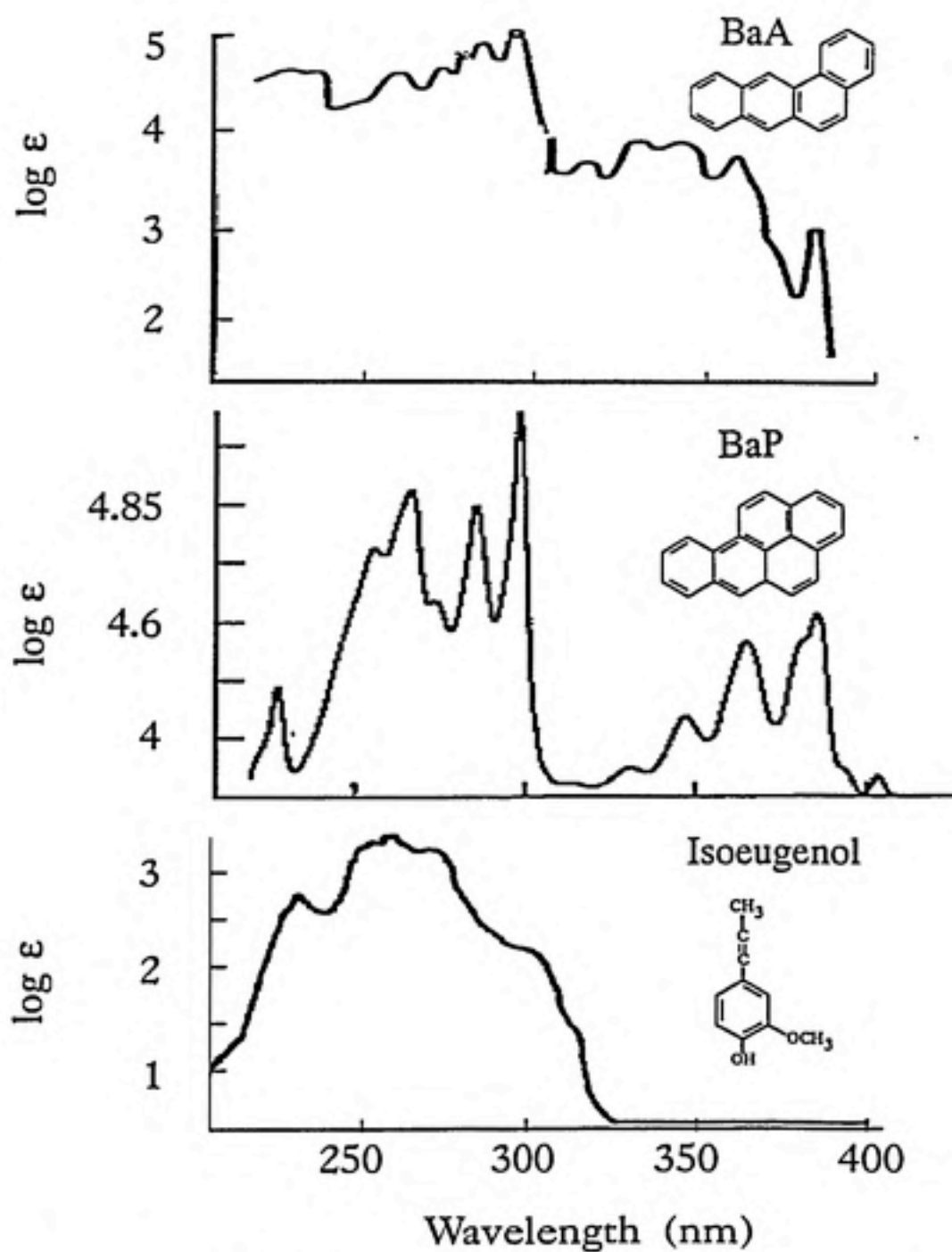


Figure 3.2. UV Absorption Spectrum of BaA and BaP from Finlayson-Pitts and Pitts, 1986 and of Isoeugenol, measured with a HP 8451A Diode Array Spectrophotometer

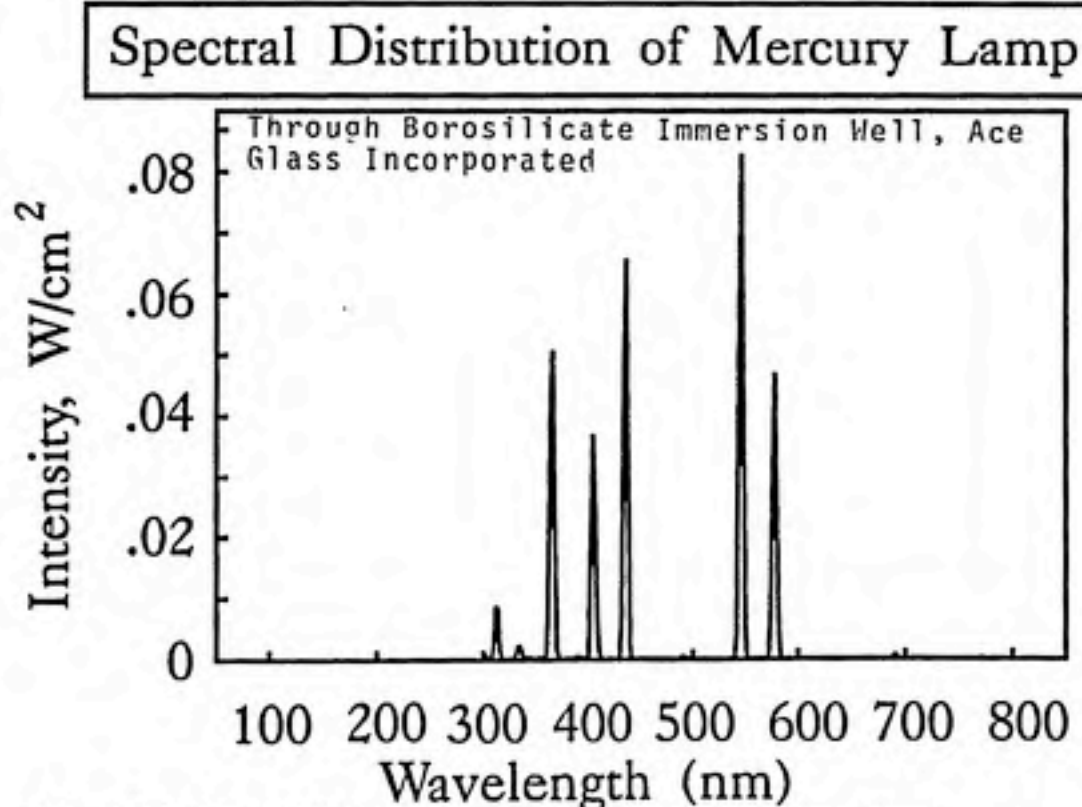
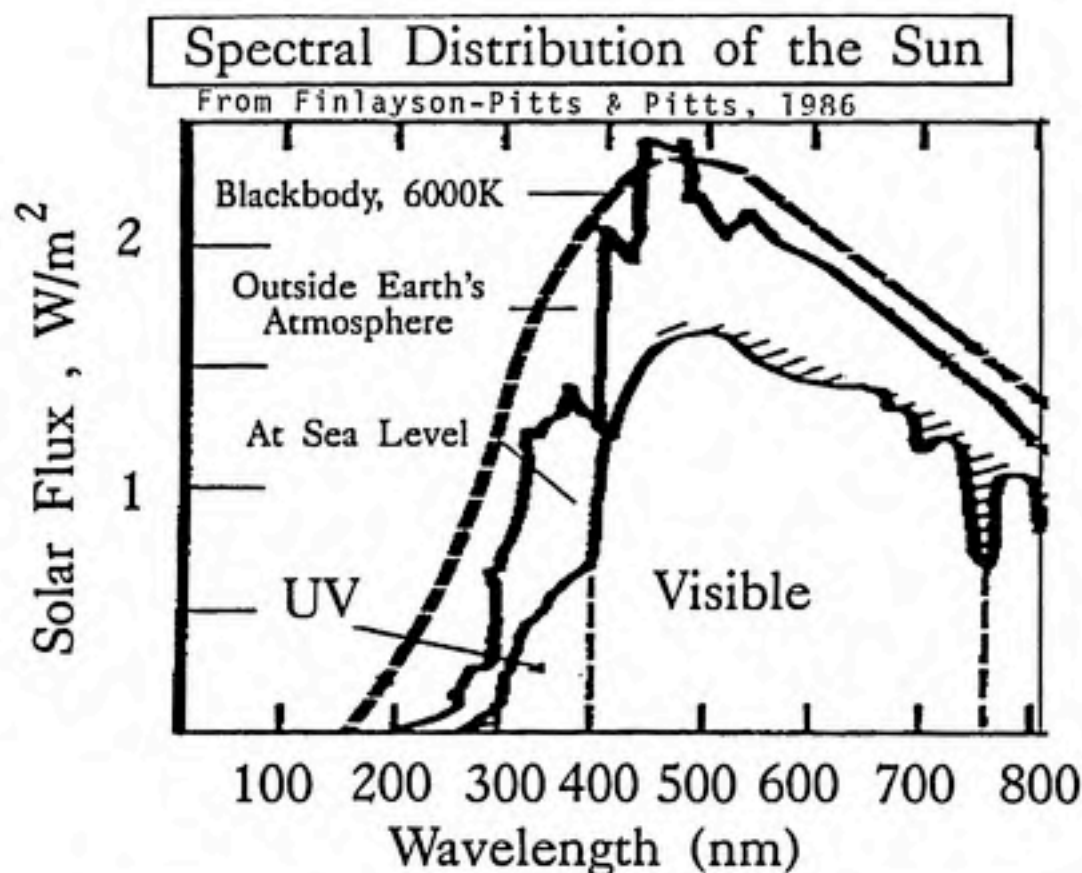


Figure 3.3. Spectral Distribution of the Sun and the Mercury Lamp

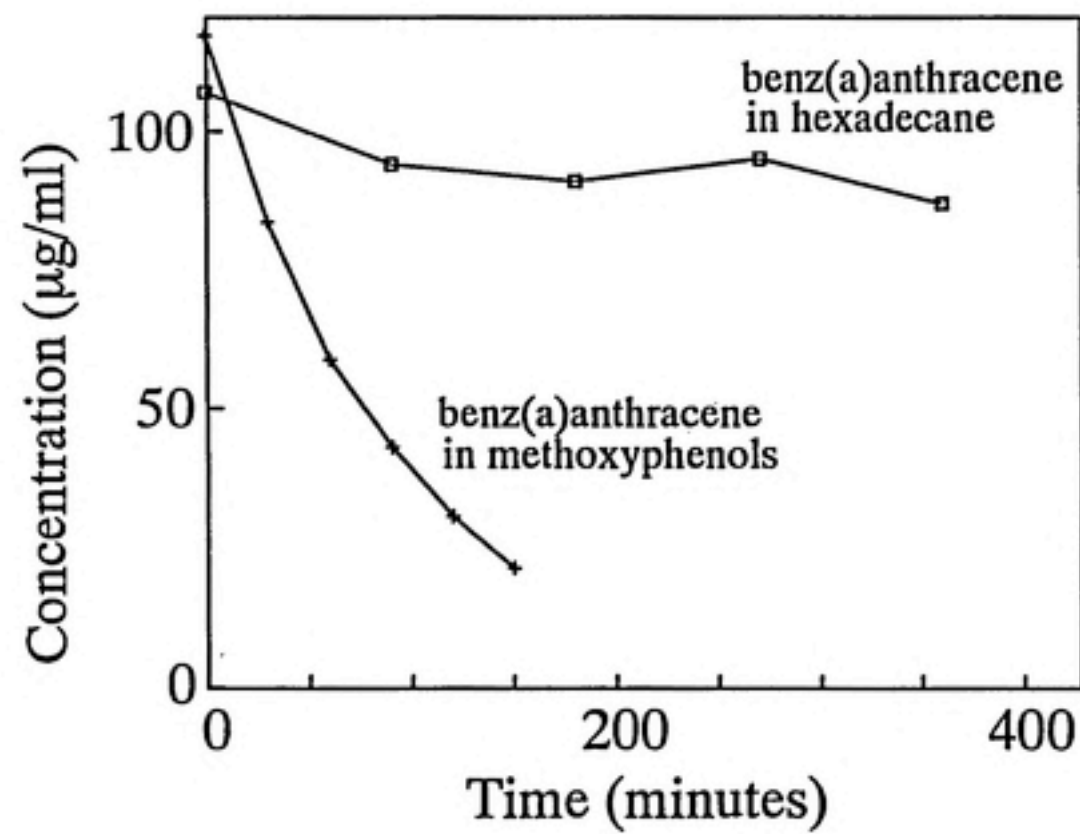


Figure 3.4. Comparison of Benz(a)anthracene photodegradation in hexadecane and in methoxyphenols from McDow et al., 1993



## 4. Results

### Summary of Experiments

There were 11 phases to the experimental work. First, PAH reactivity on filter surfaces in the dark and exposed to light was determined. Second, reactivity of PAH when coated on bare carbon black surfaces supported by filters in the dark and exposed to light was determined. Third, the influence of isoeugenol's presence with PAH in the coating of the carbon black particles supported by filters on PAH stability in the dark and exposed to light was measured. Fourth, a technique was developed for the preparation of uniform multicomponent organic coating on carbon black particles which minimized association of the coating with the filter, and maximized coating association with the carbon black surface. Fifth, PAH degradation rates on these multicomponent organic coated carbon black particles in the dark and in the light were measured. The sixth phase was geared towards product analysis of the photodegraded PAH samples as well as PAH degradation rate determination on multicomponent organic coated carbon black particles at higher isoeugenol concentrations than in the fifth phase. In the seventh phase different light filters were used including the borosilicate immersion well, and the light filters to cut out everything but 366nm wavelength. The particle surface area was measured using the BET method of analysis in phase 8. Scanning electron microscopy was performed on filter samples in phase 9. Optical and fluorescence microscopy was performed in phase 10. In the eleventh phase the particle size distribution of the coated carbon black particles was determined using an Andreasen Sedimentation Pipet.

#### 4.A First Phase

Sept 4, 1991

The purpose of this experiment was to evaluate PAH degradation in the dark for PAH deposited on Pallflex filters. The samples were placed in the turntable reactor for 3 hours, and removed for extraction and analysis at 1 hour increments. The PAH were slurry coated on to the filter (see section 3A). A syringe was used to transfer 50 $\mu$ l of NBS 1647b solution containing PAH to the filter. The concentration of PAH in the solution was 114.5 ng/ $\mu$ l. The HPLC instrument was used to analyze the extracted samples. Results are described in Table 4.1 for fluoranthene (Fl), benz(a)anthracene (BaA), benzo(k)fluoranthene(BkF) and benzo(a)pyrene (BaP). TT refers to the turntable reactor.

Table 4.1a PAH Dark Reactivity on Pallflex Filters			Table 4.1b % PAH Remaining on Filter after 3hr in Dark		
Compound	Half-life (hrs) in TT	R <sup>2</sup>	Compound	% on Filter @3hr in TT	% on Filter @3hr in box
Fluoranthene (Fl)	1.8	.99	Fl	32	77
Benz(a)anthracene, (BaA)	10	.65	BaA	79	90
Benzo(k)fluoranthene , (BkF)	27	.97	BkF	92	90
Benzo(a)pyrene (BaP)	8.7	.99	BaP	79	88

The results are shown in Tables 4.1a and 4.1b, and indicate that PAH are not reactive on the filter in the dark, and there is some loss due to blow off when placed under a vacuum when in the Turntable reactor.

September 14, 1991

The purpose of this experiment was to determine PAH photodegradation rates on Pallflex quartz fiber filters. Filter samples were irradiated for 0, .5, 1, 1.5, and 3 hrs prior to extraction and subsequent analysis. One filter was kept in the dark for 3 hours prior to extraction.

A PAH stock solution Standard #1, containing fluoranthene, benzo(a)anthracene, benzo(k)fluoranthene, and benzo(a)pyrene was prepared. Concentrations of PAH in this standard are reported in Table 5.1 (section 5B). 250 $\mu$ l of Standard #1 solution was slurry coated on to each filter. The total PAH concentration in the solution was 34.3ng/ $\mu$ l. HPLC was used to analyze the extracted samples.

Table 4.2						
PAH Photolysis Rates on Pallflex Filters						
and % PAH Remaining on Filter after Exposure to UV						
Compound	Half-life (hrs) till 1.5hr	R <sup>2</sup>	Half-life (hrs) til 3hr	R <sup>2</sup>	% on Filter @1.5hr in TT	% on Filter @3hr in TT
Fl	.48	.91	.75	.87	14	6
BaA	.55	.91	.83	.88	16	7
BkF	3.2	.77	3.5	.62	110	54
BaP	.90	.92	1.2	.94	34	16

Results in Table 4.2 suggest that Fl, BaA, and BaP are all reactive when exposed to UV light. BkF is less photoreactive then the other PAHs. PAHs were stable on the filter which was unexposed to light.

#### 4.B Second Phase

September 27, 1991

The purpose of this experiment was to determine the reactivity of PAH in solution with hexadecane adsorbed on filters containing Carbon Black, versus PAH adsorbed on bare filters in the dark. Filters were extracted for analysis at times equal to 0 hour, .5 hour, 1 hour, and 3 hours after preparation. The filters were slurry coated using 250 $\mu$ l of Standard #1 solution syringe spike, total concentration of the PAH solution was 17.5ng/ $\mu$ l, 250 $\mu$ l was applied per filter, The weight of carbon black applied to one set of the filters was 1.5mg. The mass percentage of PAH on the carbon black (CB) particles was .33%. The HPLC instrument was used to analyze the extracted samples.

Table 4.3a		
PAH Dark Reactivity on CB versus Filter		
Compound	Half-life (hrs) , on CB in TT	Half-life (hrs) on filter in TT
Fl	10	stable
BaA	5.9	32
BkF	3	stable
BaP	2.2	58

Table 4.3b			Table 4.3c	
%PAH Remaining after 3 Hours			Recovery of PAH from CB	
Compound	% on CB+Filter @3hr	% on Filter @3hr	%	
Fl	76	103	106	
BaA	69	95	51	
BkF	50	98	31	
BaP	39	107	29	

The results indicate that PAH coated on the filter are very stable, more stable than was observed in the first experiment. Reactions are referred to as stable in Table 4.3 if half-lives were much longer than the experimental duration. The results indicate that PAH have significantly shorter half-life in the dark when CB is present, but the data are more variable. Initial concentrations of PAH were much higher on the filter without CB. Recovery is the amount of PAH extracted from the carbon black divided by the amount placed on the carbon black. Even though thimbles were used in the soxhlet extractor the recovery of PAH from carbon black was low. This led to an extraction method improvement of using glass wool above and below the filter in the thimbles.

October 20, 1991

The purpose of this experiment was to measure the PAH photodegradation rates for PAH and hexadecane coated on carbon black versus coated on filters. The goal was to determine the effect of carbon black surface on the photodegradation rate of PAH. Filters were removed for extraction and analysis at .5 hour intervals for CB, 1hr intervals for hexadecane samples, with the total exposure of 3 hours for the last pair of filters. The PAH were slurry coated on the filters using a syringe to apply 250 $\mu$ l of Standard #1 solution. The concentration of PAH in solution was 313.5ng/ $\mu$ l. The



mass of carbon black applied to one set of filters was 1.0mg on each filter. The mass percentage of PAH adsorbed on the carbon black was 7.8%. The HPLC instrument was used to analyze the extracted samples. Results are presented in Table 4.4.

Table 4.4a			
PAH Photolysis Rates on Carbon Black Versus Zefluor Filter			
Compound	Half-life(hr) on CB +Hexadecane+Zefluor	R <sup>2</sup>	Half-life - on Hexadecane + Zefluor
Fl	.86	.93	<.5
BaA	.66	.92	<.5
BkF	1.3	.97	<.5
BaP	.81	.96	<.5

Table 4.4b				
% PAH Remaining After Exposure to UV Light				
Compound	% remaining on CB + Zefluor @1hr	% remaining on Zefluor @1hr	% remaining on CB + Zefluor @3hr	% remaining on Zefluor @3hr
Fl	45	19	18	5.5
BaA	26	3.4	14	5.6
BkF	64	8.6	28	8.0
BaP	41	4.5	19	7.0

PAH initially degrade quickly upon exposure, and then appear stable under continued exposure to light. PAH in hexadecane on the filter has a faster initial rate and saturates at lower concentrations than for PAHs in hexadecane on carbon black on

filters. More data are needed for PAH reactivity on hexadecane + filter at earlier times to calculate their half-lives. The presence of carbon black caused a decrease in the photoreactivity of PAH. PAHs photodegrade quickly on the filter. The observed photodegradation rate for PAH on Zefluor filters was faster than that previously observed for PAH on Pallflex filters.

November 2, 1991

The purpose of this experiment was to evaluate PAH Photodegradation on CB+Pallflex filter, CB+Zefluor filter to determine if PAH reactivity on carbon black is influenced by the filter media. Filters were analyzed at 0.5 hr intervals for a total duration of 2.5 hours for both systems. The PAH were slurry coated on to the filter, using a syringe to apply 250 $\mu$ l of Standard #1 solution to each filter. The concentration of PAH in solution was 184ng/ $\mu$ l. The weight of carbon black applied to each filter was 1.0 mg. The mass percentage of PAH on CB on Pallflex filters was 4.6%. The initial unexposed filter (t=0) was lost for the set with PAH adsorbed to carbon black on the Zelfuor filter. HPLC was used to analyze the extracted samples. Results are given in Table 4.5.

Table 4.5a				
PAH Photolysis Rates when Adsorbed on CB on Different Filters				
Compound	Half-life(hrs) CB + Pallflex	R <sup>2</sup>	Half-life(hrs) CB + Zefluor	R <sup>2</sup>
Fl	12	.41	1.8	.90
BaA	2.3	.90	1.8	.86
BkF	1.7	.94	2.1	.98
BaP	1.6	.94	0.9	.90

Table 4.5b		
%PAH Remaining after Exposure to UV light		
Compound	% remaining on CB + Pallflex @1.5hr using $t=.5$ as $t=0$	% remaining on CB + Zefluor @1.5hr, using $t=.5$ as $t=0$
Fl	96	53
BaA	69	52
BkF	75	72
BaP	42	47

Fl and BaA have longer half-lives on carbon black + Pallflex filters than carbon black + Zefluor filters, indicating that there is an effect on PAH reactivity due to the type of filter material used. The BaP and BkF half-lives observed on Zefluor and Pallflex filters with carbon black are similar. BkF and BaP may be preferentially adsorbed by the carbon black and not present as much on the filter surface. Thus, there is no effect due to using different filter surfaces to support carbon black particles for BkF and BaP adsorption. The concentration of PAH in hexadecane in this experiment is the same for the Oct 20, 1991 experiment. PAH half-lives when coated on carbon black on Zefluor filters are similar for the two experiments of Oct 20, and Nov 2, indicating reproducibility of the measurement.

#### 4.C Third Phase

November 28, 1991

In this and subsequent experiments Zefluor Teflon membrane filters were used instead of Pallflex quartz fiber filters to support the coated carbon black. The purpose of this experiment was to measure PAH Photodegradation rates for coatings with and without

Isoeugenol on CB and Zelfuor filters. Exposed filter samples were removed for extraction and analysis at 0.25hr intervals for a total exposure duration of 1 hour. The goal was to adsorb organic compounds onto the carbon black particle to achieve particle composition similar to atmospheric combustion particles. The composition was targeted to be 50% elemental carbon, 45% organic carbon, 1% PAH, and 4% Isoeugenol. Carbon black was used to represent elemental carbon. Hexadecane was used to represent organic carbon. The organic compounds were slurry coated on to the carbon black which was supported by a filter. A syringe was used to transfer 50 $\mu$ l of Standard #1 solution. The PAH concentration in the solution was 125ng/ $\mu$ l. The weight of carbon black used per filter was .8mg. The mass percentage of PAH adsorbed on the carbon black was 0.79%. The half-lives were calculated by performing a regression out to .75 hour, as the concentration of PAH remained stable between the 0.75 hour and 1 hour filter samples. HPLC was used to analyze the extracted samples. Results are given in Table 4.6.

Table 4.6a				
PAH Photolysis Rates when Adsorbed on CB with and without Isoeugenol				
Compound	Half-life(hour)	R <sup>2</sup>	Half-life(hour) (w/ isoeugenol)	R <sup>2</sup>
Fl	0.35	0.93	0.29	0.85
BaA	0.21	0.87	0.27	0.76
BkF	0.5	0.63	0.31	0.96
BaP	0.23	0.9	0.31	0.73

Table 4.6b				
% PAH Remaining on Carbon Black after Exposure				
Compound	% Remain@ .25hr	%Remain @.25hr w/ isoeugenol	% Remain@ 1hr	%Remain @1hr w/ isoeugenol
Fl	61	25	19	5
BaA	22	22	17	5
BkF	57	42	43	12
BaP	27	24	22	5

There was an observed difference in PAH reactivity due to isoeugenol for Fl, both the magnitude and shape of the photodegradation curve changes. No difference is observed between the photodegradation rates for BkF with isoeugenol and without isoeugenol. The photodegradation rates for BaA and BaP could not be determined because they are too reactive and mostly degraded within 15 min.

The question of why the degradation rates were faster than those observed in the Oct 20 experiment needs to be addressed. The PAH concentration may be 1.6 times that of Oct 20 and Nov 2. The change in photodegradation rate might be due to the use of less CB and more PAH. In previous experiments with slight differences in PAH and particle concentrations large differences in the photodegradation rates are not observed.

It was determined subsequent to this experiment that the water immersion well may have been unknowingly changed prior to this experiment. A quartz well was unknowingly used as a replacement after an accidental breakage of the borosilicate immersion well. The increase in PAH photodegradation rates could then be attributed to a reduced filtration of the light emitted from the mercury lamp caused by using a quartz versus borosilicate immersion well.



Another factor which may inhibit an observable difference in photodegradation rates due to isoeugenol is the distribution of PAH and isoeugenol between the carbon black and filter surfaces. PAH may be preferentially adsorbed to the carbon black surface, while isoeugenol may adsorb equally to the filter and carbon black surfaces. On the basis of this experiment it was concluded that an improved technique of applying the organic constituents to the carbon black surface was needed. This technique should ensure that the organic constituents are adsorbed to the particle surface and not to the filter.

#### **4.D Fourth Phase**

Jan 8, 1992

Development of a technique to adsorb organic constituents from a liquid phase onto carbon black particles was the goal of this experiment. The adsorptive ability of the carbon black was measured by determining the sorbate concentration on carbon black after coated particles were suspended into solvent, dispersed, and deposited on filter relative to the concentration in the original coating. Dependence of this recovery measurement on different methods of transferring the coated carbon black particles to the liquid phase in the Büchner funnel was also measured. Three transfer methods are compared in Table 4.7. These are referred to as the "spatula method", the "sonication method" and the "reference method". All three are described in detail in Section 3A. Dichloromethane was used as the dispersion liquid. The weight of the carbon black used was 1mg. HPLC was used to analyze the extracted samples.

Table 4.7 Recovery using methods of Transferring Coated Carbon Black Particles from beaker to liquid in Büchner Funnel				
Compound	% Recovery Sonication	% Recovery Sonication	% Recovery Spatula- Scraped	% Recovery Reference Method
Isoeugenol	0	0.02	1	0.3
Fl	1.8	1.7	2.7	5.7
BaA	7.6	7.5	9.1	12.8
BkF	21.8	23	26	26
BaP	22.3	23	27	27

Recoveries were poor but consistent. The recovery of PAH on the carbon black is greater for the higher molecular weight compounds, indicating stronger adsorption of BkF and BaP to the carbon black surface.

Jan 18, 1992

The purpose of this experiment was to measure the recovery of PAH on the carbon black as a function of the solvent chosen to disperse the coated carbon black. The PAH solubility in pentane is lower than PAH solubility in dichloromethane, therefore adsorption onto the carbon black surface should be greater in pentane. The recovery of PAH due to adsorption of PAH on the filter with no carbon black present was also measured. The technique for transferring the coated particles was to use a spatula to transfer the majority of the particles, then to sonicate and transfer any remaining particles from the walls of the glass beaker. HPLC was used to perform analysis of the extracted filter sample. Results are given in Table 4.8.

Table 4.8				
Recovery of PAH on Carbon Black using different solvents for the Liquid Dispersion Phase				
Compound	%Rec. on CB in MeCl <sub>2</sub>	%Rec on CB in Pentane	% Rec in MeCl <sub>2</sub>	% Rec in Pentane
Isoeugenol	.04	.57	0	0
Fl	3.6	5.4	0	0
BaA	8.9	24	.45	.34
BkF	16	49	.54	.50
BaP	21	54	.55	.53

Pentane is a better dispersion liquid for PAH than dichloromethane (MeCl<sub>2</sub>). The observed recovery for PAH dispersed with no carbon black to adsorb is less than 1% indicating that little adsorption on the filter occurs. The observed recovery for PAH when adsorbed on carbon black is much higher, indicating that most of the PAH remains adsorbed on the carbon black. On further study it was observed that pentane was a poor solvent for dissolution of isoeugenol at concentrations typically used in these experiments.

Jan 26, 1992

The purpose of this experiment was to determine whether the coating technique was improved if carbon black and organics were separately placed in the Buchner funnel using the "no transfer method" of Section 3A. It was hypothesized that this would obviate the step of transferring particles from the beaker where the organics were coated to the liquid phase in the Büchner funnel. The proposed ratio of constituents was 30% carbon black, 1% PAH, 40% organic carbon, and 29% Isoeugenol. The

mass of carbon black used for this experiment was 1.5 mg. HPLC was used to perform analysis of the extracted filter samples. Results are given in Table 4.9.

Table 4.9		
% Recovery for Coating in a Vial + Transferring or Adsorbing PAH in Liquid Phase		
Compound	%Recovered no transfer	%Recovered BFT
Isoeugenol	.21	.16
Fl	.83	.80
BaA	3.5	5.5
BkF	27	21
BaP	24	20

70-80% of the carbon black particles were transferred successfully when the technique of coating the particles in a vial then transferring them to the Büchner funnel was used. Only 50-70% of the carbon black particles were transferred successfully when carbon black was transferred dry to the Büchner funnel.

Feb. 1, 1992

The purpose of this experiment was to determine the reproducibility in PAH concentration observed on the coated particles using the BFT described in Section 3A, and to determine if filters were adsorbing PAH from the liquid phase. Six identical Büchner funnel filters were prepared containing organic constituents adsorbed to carbon black for extraction and analysis. Three identical filters were prepared by placing the organic compounds in the liquid phase without any carbon black, then drawing them through the filters for extraction and analysis. Two vials containing coated carbon

black were transferred directly to the soxhlet extractor to determine the extraction efficiency for removing PAH from carbon black. HPLC was used to perform analysis of the extracted filter sample.

Table 4.10				
% PAH Recovered on Carbon Black and Filter and on Filter Only				
Compound	%Recovered on CB on Zeffluor	CV, 6 samples,	%Recovered on Filter	CV, 3 samples
Isoeugenol				
Fl	1.2	8	0.17	(2 filters w/ no Fl)
BaA	5.2	27	0.42	16
BkF	26	12	0.52	12
BaP	32	14	0.49	15

Results (Table 4.10) showed good reproducibility for adsorbing organic compounds onto carbon black. The term "CV" refers to the coefficient of variation which is the percent sample standard deviation divided by the mean. Much more PAH adsorbed to Carbon Black than adsorbed on to the filter.

#### 4.E Fifth Phase

March 11, 1992

The purpose of this experiment is to determine the stability of PAH when adsorbed on carbon black with and without isoeugenol in the dark using the BFT. The samples were placed in the turntable reactor and removed at intervals of 0 hour, 1 hour, 2 hours, 2.5 hours, and 3.5 hours. The coating solution was prepared to obtain the projected coating composition of 30% carbon black, 1% PAH, 40% hexadecane, and 29% isoeugenol. The total PAH concentration adsorbed on the carbon black was



48.3ng/ $\mu$ l. The sample solutions were applied and analyzed in volumes of 250 $\mu$ l. The weight of carbon black used on each filter was 1.45 mg. The mass percentage of PAH adsorbed to the carbon black was .81 %. The mass percentage of isoeugenol adsorbed to the carbon black was .9% (much less than desired). To achieve the adsorbed organic composition the solution contained 20.7  $\mu$ l of hexadecane, and 10.8  $\mu$ l isoeugenol, in addition to 2 ml of Standard #1 solution (2 x conc.). HPLC was used to perform analysis of the extracted filter sample. Results are given in Table 4.11.

Table 4.11				
PAH Reactivity in the Dark on Carbon Black Adsorbed w/ + w/out Isoeugenol using BFT				
Compound	Half-life (w/o iso) (hr)	Half-life (w/ iso)(hr)	%PAH remaining (w/o iso)	%PAH remaining (w/iso)
Isoeugenol		1.8		1.3
Fl	9.7	5.9	82	65
BaA	21	24	86	92
BkF	18	76	83	101
BaP	25	172	86	102

Isoeugenol apparently decayed with a 1.8 hour half-life, this may have been due to evaporation from the surface. The results indicate that some PAH may be more stable in dark when isoeugenol is coadsorbed on the carbon black surface.

March 26, 1992

The purpose of this experiment was to measure the photodegradation rate of PAH coated either with isoeugenol or without isoeugenol on carbon black prepared by the BFT. Filter samples were extracted at 0.5 hour intervals over a 2 hour exposure period. The PAH concentration obtained on the carbon black was 18.9 ng/ $\mu$ l which

was applied and analyzed in 250 $\mu$ l of solvent. The weight of carbon black used on each filter was 1.5 mg. The mass percentage of PAH adsorbed on to the carbon black was .32%. The mass percentage of isoeugenol adsorbed on to the carbon black was .9%. To achieve the desired adsorbed organic composition the solution contained 20.7  $\mu$ l of hexadecane, and 10.8  $\mu$ l isoeugenol, in addition to 2 ml of Standard #1 solution (2 x conc.). HPLC was used to perform analysis of the extracted filter sample.

Table 4.12				
Influence of Isoeugenol on Photolysis Rate of PAH coated on CB				
Compound	Half-life(hr)	R <sup>2</sup>	Half-life(w/ iso)(hr)	R <sup>2</sup>
Isoeugenol				
Fl	4.0	.25	9.9	.17
BaA	6.8	.52	6.8	.31
BkF	11	.37	12	.16
BaP	4.6	.83	4.5	.63

Table 4.12a				
% PAH Remaining on the filter after Exposure to UV Light				
Compound	% Remain@ .5hr	%Remain @.5hr w/ isoeugenol	% Remain@ 2hr	%Remain @2hr w/ isoeugenol
Fl	70	126	60	99
BaA	81	87	81	72
BkF	92	104	90	83
BaP	80	107	70	72

The results (Table 4.12) indicate that the PAH are stable both in the presence and absence of isoeugenol. This result is not consistent with the November 28 slurry coating experiment in which each PAH reacted rapidly. No difference due to the presence of isoeugenol was detected. It was speculated that the observed stability was due to the low PAH concentration on the particle. A fraction of the PAH might be strongly bound to the particle surface and unavailable for light absorption or photodegradation. This fraction is expected to decrease with increasing total PAH concentration. The PAH may be inside the pores of the carbon black and shielded from radiation. It is possible that the concentration of isoeugenol adsorbed on the particle surface was also too low. The next experiments were analyzed using GCMS to detect the photodegradation products of isoeugenol.

April 20, 1992

The purpose of this experiment was to repeat the March 26 experiment using higher isoeugenol concentrations (6-9 times higher). Filter samples were extracted at .5 hour intervals over a 1.5 hour exposure period. The BFT technique was used to prepare the particles. The PAH concentration obtained on the carbon black was 14.4 ng/ $\mu$ l which was applied and analyzed in 250 $\mu$ l of solvent. The weight of carbon black used on each filter was 1.5 mg. The mass percentage of PAH adsorbed on carbon black was 0.24 %. The mass percentage of isoeugenol adsorbed on the carbon black was 2.6%. To achieve the adsorbed organic composition the solution contained 40 $\mu$ l of hexadecane, and 60 $\mu$ l isoeugenol, in addition to 2 ml of Standard #1 solution (2 times concentrated). GCMS and HPLC were used to perform analysis of the extracted filter samples. Results from GCMS data are reported in Table 4.13 (HPLC and GCMS data were consistent).

Table 4.13 Influence of Isoeugenol on Photolysis Rate of PAH on CB, and % PAH Remaining after Exposure to UV Light						
Compound	Half-life (hr)	R <sup>2</sup>	Half-life w/ Isoeugenol (hr)	R <sup>2</sup>	%Rem	%Rem w/iso
Isoeugenol			0.28	.57		1.2
Hexadecane	0.29	.99	0.25	0.88	2.9	0.68
Fl	5.1	.30	0.58	0.98	65	7.9
BaA	0.32	.53				
BkF	4.4	.01	3.4	.005	54	36
BaP						

The data obtained had serious problems with variability, BaA, and BaP are not consistently detected on the extracted samples. The amount of PAH measured on each sample is subject to error during the extraction procedure, the CB coating procedure and during exposure to light when mounted in the turntable reactor. The results indicate that fluoranthene reacts faster in isoeugenol. This experiment indicated the need to use the GC-MS to analyze for product formation, to determine what happens to the isoeugenol. PAH when coadsorbed with a higher concentration of isoeugenol than that used in March 26th experiment is observed to be more photoreactive.

May 14, 1992

The purpose of this experiment was to repeat the March 26 and April 20 experiments using a shorter time interval for exposure. The goal was to measure the initial photodegradation rate, as the rate may change as products form and change the adsorbed organic layer properties. Filter samples were extracted at .25 hour intervals over a 1 hour exposure period. The PAH concentration obtained on the carbon black

was 14.4 ng/ $\mu$ l which was applied and analyzed in 250  $\mu$ l of solvent. The weight of carbon black used on each filter was 1.5 mg. The mass percentage of PAH adsorbed onto carbon black was 0.24%. The mass percentage of isoeugenol adsorbed on the carbon black was 2.6%. To achieve the adsorbed organic composition the solution contained 40 $\mu$ l of hexadecane, and 60 $\mu$ l isoeugenol, in addition to 2 ml of Standard #1 solution (2 x conc.). The GC-MS and HPLC instruments were used to perform analysis of the extracted filter samples. Results from GC-MS data are reported in Table 4.14 (HPLC and GC-MS data were consistent).

Table 4.14 Influence of Isoeugenol on Photolysis Rate of PAH on CB, and % PAH Remaining after Exposure						
Compound	Half-life (hr)	R <sup>2</sup>	Half-life with Isoeugenol	R <sup>2</sup>	%Remain	%Remain w/ isoeugenol
Isoeugenol	0.29	0.53	0.26	0.79	16	23
Hexadecane	0.41	0.75	0.37	0.99	29	17
Fl	1.5	0.23	0.79	0.59	90	40
BaA						
BkF	9.6	0.29	1.8	0.52	97	67
BaP	3.1	0.27	3.2	0.02	78	57

The data indicate that trace amounts of isoeugenol were present even in the particle samples not coated with isoeugenol, due to contamination caused by using the wrong Büchner funnel. The fraction of PAH remaining after exposure indicate that the PAH reacted faster when isoeugenol was present. R<sup>2</sup> values indicate a high degree of variability in the data. Unexposed filter samples suggest that PAH adsorbed with isoeugenol on the carbon black was lost during the extraction procedure. Variability in



the data from this experiment prompted an investigation of the reproducibility of exposed filter samples. BaA concentrations were not measured on either filters, and may have been present at concentrations too low to detect.

#### May 24

The purpose of this experiment was to determine the reproducibility of exposed filter samples, which may be poor if particles are lost in the turntable reactor during exposure to light. PAH photodegradation with isoeugenol present on the carbon black was measured. Three identical filter samples for each exposure interval were prepared using the BFT. Filters were extracted at 0.25 hour intervals over a 0.75 hr exposure duration. The PAH concentration obtained on the carbon black was 26.6 ng/ $\mu$ l which was applied and analyzed in 250  $\mu$ l of solvent. The weight of carbon black used on each filter was 1.5 mg. The mass percentage of PAH adsorbed on carbon black was 0.44%. The mass percentage of isoeugenol adsorbed on carbon black was 5.2%. To achieve the desired adsorbed organic composition the solution contained 80  $\mu$ l of hexadecane, and 120  $\mu$ l isoeugenol, in addition to 4 ml of Standard #1 solution (2 x conc.). GCMS and HPLC were used to perform analysis of the extracted filter samples. Results from GCMS data are reported in Table 4.15. (HPLC and GCMS data were consistent). Half-lives are reported as "short" if most of the compound had reacted after the first time interval.

Table 4.15a			
Reproducibility of adsorbed [PAH] on Exposed Filter Samples			
Compound	Avg [PAH] ng/ $\mu$ l	CV at t=0 3 samples	CV at t=.75 hr 2 samples
Isoeugenol		41	34
Hexadecane		27	40
Fl	2.6	27	22
BaA	5.8	11	9
BkF	4.7	2.0	11
BaP	6.1	0.46	8

Table 4.15b		
PAH Photolysis Rate on CB w/ Isoeugenol		
Compound	Half-life (hr) w/ isoeugenol	R <sup>2</sup>
Isoeugenol	short	0.80
Hexadecane	0.21	0.95
Fl	0.7	0.58
BaA	1.2	0.82
BkF	2.5	0.76
BaP	1.9	0.87

Table 4.15c		
% PAH Remaining after Exposure		
Compound	% Remain@ .25hr w/ isoeugenol	%Remain @.75hr w/ isoeugenol
Isoeugenol	1.3	1.3
Hexadecane	30	7.8
Fl	42	42
BaA	71	61
BkF	85	78
BaP	84	73

The isoeugenol has was low after 15 min, most of it reacting prior to analysis of the first sample. Poor reproducibility was observed for isoeugenol concentrations on the

unexposed filters. PAH appears to stop reacting after isoeugenol is gone. The available data indicate that PAH reacts quickly when isoeugenol is present. The reproducibility of the PAH concentration found on the carbon black on filters exposed to identical amounts of light is good, although the relative standard deviation seems to increase with decreasing molecular weight.

#### 4.F Sixth Phase

June 19

The purpose of this experiment was to use duplicate filters for each exposure time to determine the influence of isoeugenol on the PAH photodegradation rate. Filters were extracted at 0.5 hour intervals over a 1.5 hr exposure duration. The BFT was used to prepare the particles. A second standard stock solution was prepared (Standard #2). Concentrations of PAH in the standard solution are reported in Table 5.1 (Section 5B). The PAH concentration obtained on the carbon black was determined to be 35.1 ng/ $\mu$ l which was applied and analyzed in 400  $\mu$ l of solvent. The weight of carbon black used on each filter was 1.5 mg. The mass percentage of PAH adsorbed on carbon black was 0.94%. The mass percentage of isoeugenol adsorbed on carbon black was 3.5 %. To achieve the adsorbed organic composition the solution contained 80  $\mu$ l of hexadecane, and 120  $\mu$ l isoeugenol, in addition to 4 ml of Standard #2 solution. GCMS and HPLC were used to perform analysis of the extracted filter samples. Results from GCMS data are reported in Table 4.16 (HPLC and GCMS data were consistent).

Table 4.16a				
Influence of Isoeugenol on Photolysis Rate of PAH on CB				
Compound	Half-life (hr)	R <sup>2</sup>	Half-life w/ isoeugenol (hr)	R <sup>2</sup>
Isoeugenol			0.21	0.81
Hexadecane	0.44	0.62	0.40	0.85
Fl	1.4	0.43	1.2	0.64
BaA	1.6	0.59	1.6	0.71
BkF	1.9	0.58	2.6	0.78
BaP	1.2	0.86	1.7	0.93

Table 4.16b						
Initial Concentration of PAH and % PAH Remaining after Exposure						
Compound	[PAH] ng/ml	[PAH] w/ iso, ng/ml	% Remain @ .5hr	%Remain @.5hr w/ isoeugenol	% Remain @ 1.5hr	%Remain @1.5hr w/ isoeugenol
Isoeugenol				2.1		0.55
Hexadecane			11	15	5.2	6.45
Fl	11	11	37	38	41	37
BaA	9.0	7.4	51	52	49	50
BkF	8.0	6.2	57	66	55	67
BaP	13	10	56	66	39	50

Most of the isoeugenol reacted before the first exposed filter sample at 0.5 hour. The concentration of hexadecane also decreased rapidly within 0.5 hr. It appears that the PAH degraded slightly faster with no isoeugenol present, contrary to what was expected and contradicting earlier experiments. The only difference with this experiment was that the PAH concentration was higher. Initially PAH reacts quickly, declining 50% in .5 hr. PAH then seem stable in both systems. The remaining PAH may not be available for photodegradation.

These samples were analyzed on the GCMS in full ion scan, and injected directly on-column in order to identify major products formed in the photolysis of the multicomponent organically coated carbon black particles. The major products characterized from possible isoeugenol reaction in the organic coating were vanillin and dehydrodiisoeugenol (see Figure 4.1). The only PAH photodegradation product characterized was benz(a)anthracene-7,12-dione (Figure 4.1).

#### July 18

The purpose of this experiment was to determine the influence of isoeugenol when coadsorbed with PAH on the carbon black on the PAH photodegradation rate. The concentration of isoeugenol was increased in the coating solution, to guarantee that isoeugenol was present on the carbon black surface with the PAH. Filters were extracted at ~ 0.5 hr intervals for 1.5 hr exposure duration. The BFT was used to prepare the particles. The PAH concentration obtained on the carbon black was 35 ng/ $\mu$ l which was applied and analyzed in 500  $\mu$ l of solvent. The weight of carbon black used on each filter was 1.5 mg. The mass percentage of PAH adsorbed on carbon black was 1.2%. The mass percentage of adsorbed isoeugenol was 43%. To achieve the adsorbed organic composition the solution contained 1ml isoeugenol, in addition to 4 ml of Standard #2 solution. The GCMS and HPLC instruments were

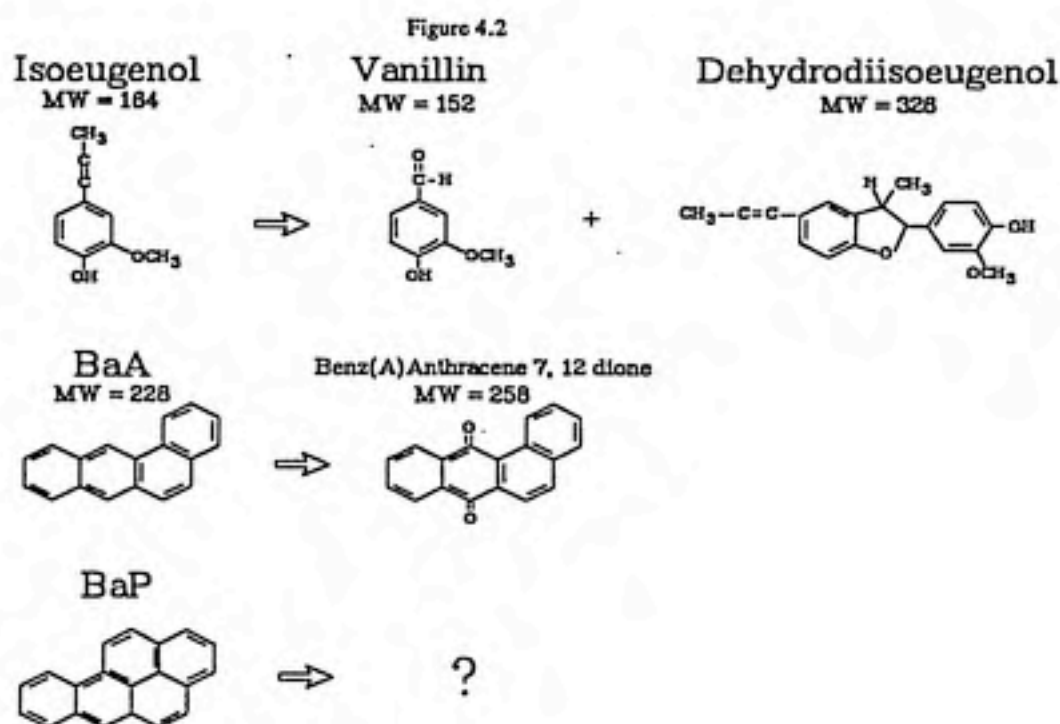


used to perform analysis of the extracted filter samples. Results from GC-MS data are reported in Table 4.17 (HPLC and GCMS data were consistent).

Table 4.17						
Influence on PAH Photolysis Rate on CB due to Isoeugenol + % PAH						
Remaining after Exposure						
Compound	Half-life (hr)	R <sup>2</sup>	Half-life with isoeugenol (hr)	R <sup>2</sup>	% Remain @ .75hr	%Remain @.75hr w/ isoeugenol
Isoeugenol						
Fl	2.0	0.79	0.58	0.83	59	17
BaA	1.47	0.25	1.3	0.97	49	52
BkF	3.41	0.31	5.4	0.91	59	86
BaP	—	—	4.5	0.89	0	90

The results indicate that Fl reacts faster, and BkF reacts slower in the presence of isoeugenol versus no isoeugenol filter samples. More variability was observed in the PAH concentrations for filters supporting carbon black coated with PAH only. The lower R<sup>2</sup> value indicating the fit of the data points to a straight line in this experiment reflects that higher variability. Almost all of the isoeugenol disappeared in the first 45 minutes. BaP was not observed on the carbon black filters which had only PAH and no isoeugenol adsorbed on them. Each of the PAHs degraded significantly before the first exposure data point at 0.75 hr. Then the reaction slowed, indicating the need for information at shorter time intervals between samples.

These samples were also analyzed for products. The same major products were characterized as found in June 19th experiment. The structures are illustrated below in figure 4.1. Procedures for compound identification are described in Section 5F.



#### 4.G Seventh Phase

August 11

The purpose of this experiment was to observe PAH photodegradation for PAH only or PAH+isoeugenol adsorbed on carbon black when exposed to atmospherically relevant wavelengths above 290 nm. A borosilicate well was used to replace the quartz immersion well which was improperly used for a series of earlier experiments (~Nov. 28-July 18). Reactions appeared to be too rapid to allow measurement of reaction rates in the previous experiments of Phases 5 and 6 in which the quartz immersion well was used. This suggested that shorter exposure times should be used. However, when the borosilicate immersion well was used the most energetic wavebands from the mercury lamp were filtered out and light intensity was less than when the quartz immersion well was used. Consequently reaction rates could still be measured with long exposure times when the borosilicate immersion well was used. Filters were

extracted at ~ 0.5 hr intervals for 1.5 hr exposure duration. The Büchner funnel filtration technique was used to prepare the particles. The PAH concentration obtained on the carbon black was determined to be 3.25 ng/ $\mu$ l which was applied and analyzed in 400  $\mu$ l of solvent. The weight of carbon black used on each filter was 1.5 mg CB. The mass percentage of PAH adsorbed on carbon black was 0.087%. The mass percentage of adsorbed isoeugenol was 21.5 %. To achieve the desired adsorbed organic composition the solution contained 500  $\mu$ l isoeugenol, in addition to 4 ml of Standard #2 solution. GCMS and HPLC were used to perform analysis of the extracted filter samples, and results from GCMS data are reported in Table 4.18a.

Table 4.18a				
PAH Photolysis Rate on CB due to Isoeugenol using				
Borosilicate Well				
Compound	Half-life (hr)	R <sup>2</sup>	Half-life (hr) w/isoeugenol	R <sup>2</sup>
Isoeugenol			0.39	0.79
Fl	2.5	0.51	0.99	0.66
BaA	stable	0.16	2.6	0.41
BkF	stable	0.03	6.7	0.31
BaP			2.8	0.78

Table 4.18b				
% Remaining on Filter after Exposure to Atmospherically Relevant Wavelengths				
Compound	% Remain@ .5hr	%Remain @.5hr w/ iso	% Remain@ 1.5hr	%Remain @1.5hr w/iso
Isoeugenol		14		7
Fl	65	38	62	33
BaA	123	63	78	64
BkF	102	87	106	87
BaP	0	82	0	73

The data for BaP obtained in samples which did not include isoeugenol in the adsorbed layer was poor again. Either BaP was not being recovered from the carbon black or it was reacting immediately. The data indicate that PAH other than BaP react faster when isoeugenol is present. The initial rate of reaction is difficult to determine from these data because most of the reactivity occurred before the first exposure sample at .5 hour. In contrast to previous experiments, initial reaction rates were easily measured with the borosilicate immersion well because the UV light was less energetic and had lower intensity than when the quartz immersion well was used. On the basis of this experiment a new standard stock solution (Standard #3, see Table 5.1) was prepared to ensure that the BaP results were not due to degradation of the stock solution. Results also indicate that significantly less PAH is reacting on the particles using the borosilicate lamp immersion well than was observed when the quartz immersion well was used.

August 26

The purpose of this experiment was to determine the recovery of PAH and isoeugenol on the carbon black + filter versus filter only when a high PAH and isoeugenol coating concentration was placed on the carbon black and the particles dispersed in the liquid phase. A third standard stock solution was prepared for this experiment. To achieve the desired adsorbed organic composition 5  $\mu$ l of isoeugenol and 400  $\mu$ l of Standard #3 was used to coat each mg of carbon black. Results are given in Table 4.19.

Table 4.19			
% PAH Recovered on Carbon Black and Filter and on Filter Only			
Compound	%Recovery on 1.5mg CB on Zefluor	%Recovery on 1.0mg CB Zefluor	%Recovery on Zefluor
Isoeugenol	0.2	1.0	1.7
Fl	1.1	1.5	1.7
BaA	2.1	2.0	1.6
BkF	3.7	3.1	1.3
BaP	4.8	3.9	1.3

Only the PAH of higher molecular weight show evidence of being adsorbed by the carbon black in greater concentration than adsorbing on the filter alone. Most of the PAH in the highly concentrated stock solution were washed through the filter, and only the amount of PAH which the surface of the carbon black and filter was able to retain was recovered. This suggests that the stock solution should not be as concentrated in future experiments. In this experiment, dichloromethane was the solvent used to disperse the coated carbon black particles. It was the only solvent which was miscible with both isoeugenol and PAHs. However, this liquid may compete with the coating



compounds for the carbon black surface, or the coating compounds are more likely to dissolve in the solvent than to remain on the carbon black surface.

August 28

The purpose of this experiment was to measure the PAH photodegradation rate for PAH only or PAH + isoeugenol adsorbed on carbon black particles. A quartz immersion well with light filters was installed. This reduced the light intensity 90% by filtering all wavelengths except the 366 nm emission band from the Hg lamp. Filters were extracted at 0.75 hour intervals for a total 3 hour exposure duration. The BFF technique was used to prepare the particles. The PAH concentration obtained on the carbon black was determined to be 27 ng/ $\mu$ l which was applied and analyzed in 400  $\mu$ l of solvent. The weight of carbon black used on each filter was 1.0 mg. The mass percentage of PAH adsorbed on carbon black was 1.08%. The mass percentage of adsorbed isoeugenol was 16%. To achieve the adsorbed organic composition the solution contained 250  $\mu$ l isoeugenol, in addition to 3 ml of Standard #3. GCMS and HPLC were used to perform analysis of the extracted filter samples. Results from GCMS data are reported in Table 4.20.

Table 4.20						
Influence of Isoeugenol on Photolysis Rate of PAH on CB using Optical Filters, and % Remaining on Filter after Exposure						
Compound	Half-life w/o isoeugenol (hr)	R <sup>2</sup>	Half-life with isoeugenol (hr)	R <sup>2</sup>	% Remain @ 3hr w/o isoeugenol	%Remain @3hr w/ isoeugenol
Isoeugenol			0.77	0.75		11
Fl	2.8	0.78	5.0	0.46	56	70
BaA	8.4	0.68	8.6	0.76	81	85
BkF	37	0.2	4.9	0.72	100	68
BaP	27	0.21	5.5	0.87	98	73

The data indicate that BkF and BaP are reacting faster in the presence of isoeugenol. A significant amount of the adsorbed PAH remains unreacted on the carbon black both in the presence and absence of isoeugenol. The fraction of fluoranthene remaining on the carbon black surface after 3 hours is high. This indicates either that the loss of fluoranthene observed in previous experiments probably should not be attributed to loss due to volatilization or that volatilization is not important when isoeugenol is present. On the basis of these results an experiment of longer exposure time duration was planned to determine the behavior of the adsorbed PAH under continued exposure to light.

Sept 9

The purpose of this experiment was to extend the time over which filter samples were exposed to a total of 6 hours, as a shorter experiment resulted in degradation of only 10-20% of the adsorbed PAH. The goal was to measure the PAH photodegradation rate for PAH only or PAH+Isoeugenol adsorbed on carbon black particles. As in the previous experiment, a quartz immersion well with light filters was installed which reduced the light intensity 90% by filtering out all emission bands except 366 nm from the Hg lamp. Filter samples were extracted at 1.5 hour intervals for a total 6 hour exposure duration. The BFF technique was used to prepare the particles. The PAH concentration obtained on the carbon black was 55.7 ng/ $\mu$ l, which was applied and analyzed in 400  $\mu$ l of solvent. The weight of carbon black used on each filter was 1.5 mg. The mass percentage of PAH adsorbed on carbon black was 1.48%. The mass percentage of adsorbed isoeugenol was 10%. To achieve the desired adsorbed organic composition the solution contained 250  $\mu$ l isoeugenol, in addition to 3 ml of Standard #3 solution. GCMS and HPLC were used to perform analysis of the extracted filter samples, results from GCMS data are reported in Table 4.21. The photodegradation curves for BaP and BaA adsorbed on carbon black with and without isoeugenol are plotted as  $C/C_0$  versus time in Figures 3.3a and 3.3b respectively.

Table 4.21						
Influence of Isoeugenol on Photolysis Rate of PAH on CB using Optical Filters and % Remaining on Filter after Exposure to Atmospherically Relevant Wavelengths						
Compound	Half-life (hr)	R <sup>2</sup>	Half-life with isoeugenol (hr)	R <sup>2</sup>	% Remain@ 4.5hr	%Remain @4.5hr w/iso
Isoeugenol			3.0	0.39		24
Fl	7.3	0.40	3.7	0.97	55	45
BaA	18	0.35	5.6	0.96	77	59
BkF	37	0.01	11.7	0.90	97	78
BaP	stable	0.28	13.6	0.88	105	81

The 6 hour sample for the filter with isoeugenol coadsorbed on the carbon black was lost during extraction. The data indicate that PAH react faster in the presence of isoeugenol adsorbed on the carbon black (figure 4.2a,b). The enhancement of PAH reactivity due to isoeugenol is not as great as what was observed for PAH reactivity enhancement due to isoeugenol in solution (McDow et al., 1991, 1992). One possible explanation of this result is that the carbon black surface stabilizes the PAH which are adsorbed onto its surface.

Figure 4.3a

BENZ(A)PYRENE  
PHOTODEGRADATION ON  
TAILORED PARTICULATE MATRICES

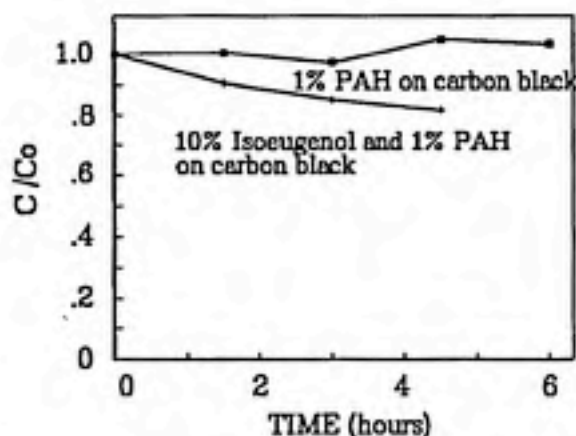
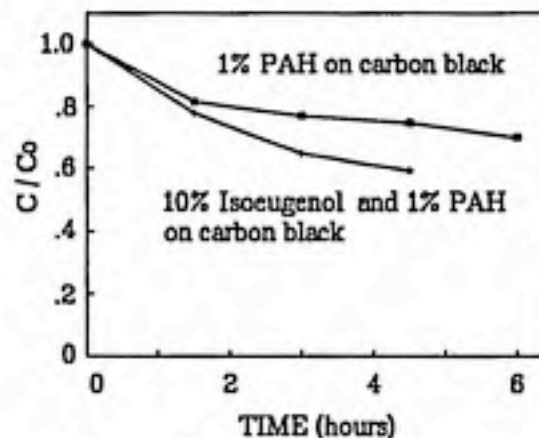


Figure 4.3b

BENZ(A)ANTHRACENE  
PHOTODEGRADATION ON  
TAILORED PARTICULATE MATRICES



#### 4.H Eighth Phase

##### Particle Characterization

BET surface area analysis was obtained by sending samples to Micromeritics

Instrument Corporation for analysis. The measured value of the BET surface area of the carbon black particles was  $95.5 \text{ m}^2/\text{g}$ . Diesel soot particles have a surface area in  $80\text{-}112 \text{ m}^2/\text{g}$  range.

#### 4.I Ninth Phase

The Scanning Electron Microscopy pictures of the particles which included PAH and isoeugenol adsorbed on the carbon black were used to estimate the particle mass median diameter of the coated particles. The results indicated that the mass median diameter of the particles was  $d_{\text{mmid}} = 12.5 \mu\text{m}$ , with a geometric standard deviation of  $s_g = 1.7$  (Figure 4.4).

The photographs also verified that isoeugenol was present on the carbon black filters. In addition the photographs showed that use of too much isoeugenol caused it to coat both the filters and the particles.

#### 4.J Tenth Phase

The optical and fluorescence microscopy photographs showed that PAH would distribute itself in the isoeugenol phase in preference to the hexadecane phase, as the two solvents were immiscible. In addition a few photographs were interpreted to show that isoeugenol kept the PAH in the liquid layer above the carbon black surface. Pictures of PAH coated on bare carbon black did not show any fluorescence, whereas pictures of PAH coated with isoeugenol on carbon black did capture the fluorescence of PAH. This could suggest that either the PAH on bare carbon black was shielded by the carbon black from absorbing the UV light preventing fluorescence, or the carbon black effectively prevented the fluorescence which was emitted from being received by the microscope.

#### 4.K Eleventh Phase

The Andreasen Sedimentation Pipet was used to determine the particle size distribution of coated carbon black particles using dichloromethane as the liquid in which the particles settled. The mass median diameter was measured to be  $d_{med}=12.5\mu m$ , with a geometric standard deviation of  $s_g=3.4$  using a log probability plot and assumption of a log normal distribution (see Figure 4.3). Comparison of these results with the distribution determined using the SEM photographs suggests that a larger range of particle sizes was measured using this technique. The major limitation of using the SEM pictures to measure the particle distribution was that small particles could not be distinguished from the filter material in the background of the pictures. The large distribution of particle sizes as indicated by the settling technique is possible, as carbon



black particles are believed to be made up of nanometer size aggregates which form large particles.

The external specific surface area may be calculated using equation 4.1.

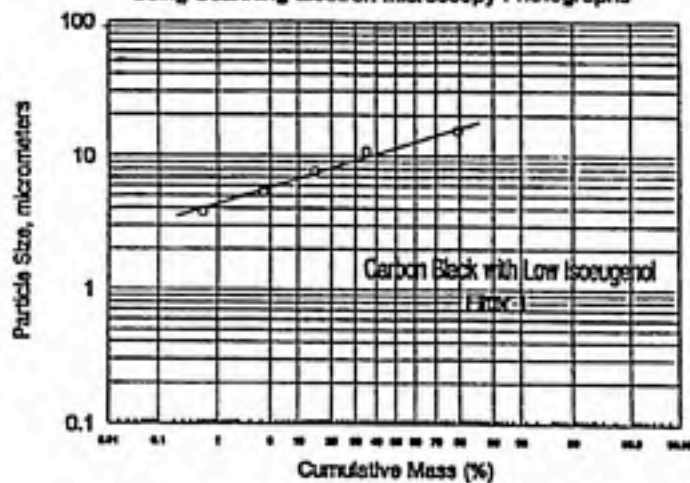
$$S_{ext} = 6/(r \cdot d_{mmd}) \quad \text{eq. 4.1}$$

where  $S_{ext}$  is the external specific surface area,  $r$  is the particle density (assumed to be  $2.0 \text{ g/cm}^3$ ) (Ross et al., 1982),  $d_{mmd}$  is the mass median diameter of the particles.

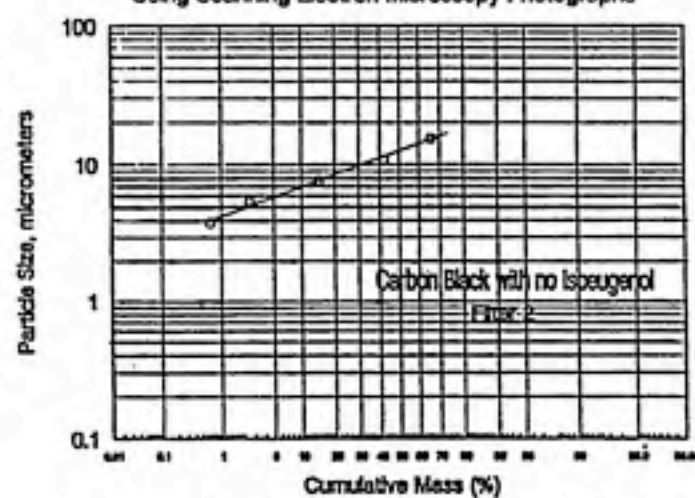
Using this equation the external surface area was determined to be  $3 \text{ m}^2/\text{g}$ . This value for the external surface area is much lower than the BET surface area of  $95.5 \text{ m}^2/\text{g}$ .

This calculated external surface area was determined by measuring the diameters of agglomerated carbon black particles. The surface area measured using the BET technique is more representative of the surface area available to PAH assuming that the size of the pores within the carbon black is larger than the PAH molecular diameter. The surface area within the agglomerated particles therefore may still be available for adsorption by the PAH and isoeugenol.

Carbon Black Particle Distribution by Mass  
Using Scanning Electron Microscopy Photographs



Carbon Black Particle Distribution by Mass  
Using Scanning Electron Microscopy Photographs



Carbon Black Particle Distribution by Mass  
Using Andraesen Sedimentation Pipet

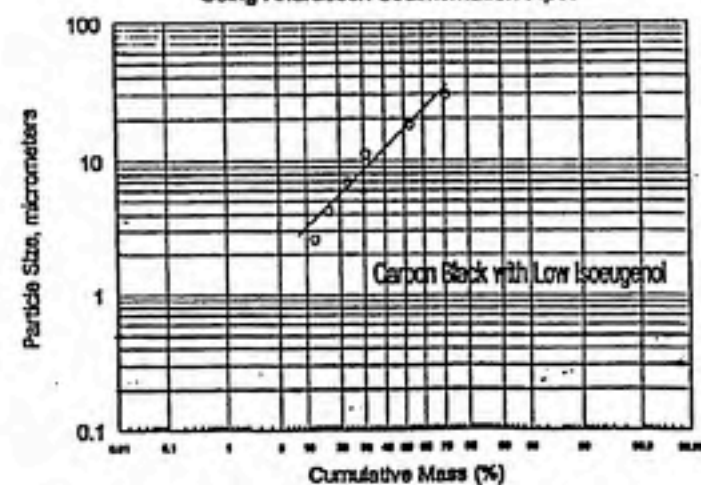


Figure 4.4. Log Probability Graphs of Carbon Black Particle Size Distribution

## 5. Discussion

Development of the method described in this study involved consideration of the following factors: particle surface characteristics, composition and concentration of organic constituents, the liquid dispersion coating technique, PAH stability in the dark, adsorbed organic concentrations, reproducibility, and UV exposure source.

### 5.A Particle surface

Current theory suggests that combustion particles, although varying in composition, consist of an elemental carbon core surrounded by an adsorbed organic layer (McDow et al., 1991, 1992). The influence of different particle surfaces on the photoreactivity of adsorbed PAH has been investigated by Behymer and Hites (1985). The chemical and physical properties of carbon black are judged to be the most representative of the elemental carbon present in combustion particles (Ross et al., 1982). The physicochemical properties of diesel combustion particles were found by Ross & Risby to be similar to graphitized carbon black when adsorption isotherms were measured (Ross et al., 1982). The BET surface area and heats of adsorption as a function of adsorbate concentration were found to be most similar for the diesel particles which had less material sorbed on them (Ross and Risby, 1982). Their BET surface area was calculated as 80 to 112 m<sup>2</sup>/g for the diesel soot, while the carbon black used in their studies had a surface area of 80 m<sup>2</sup>/g (Ross et al., 1982).

The BET surface area for the carbon black used in these experiments was measured as 95.5 m<sup>2</sup>/g. Calculation of the concentration of PAH which would exist as a monolayer on the surface can be performed from the amount of surface area required

to accommodate each sorbed molecule. The molecular surface area values were obtained from a calculation by Pankow (1987) as being  $\sim 3.8 \times 10^{-15} \text{ cm}^2 / \text{molecule}$ , for a wide range of compounds including PAH and organochlorine compounds. Assuming this molecular surface area for BaP, and using the BET carbon black surface area of  $95.5 \text{ m}^2/\text{g}$ , the amount of BaP which may be adsorbed on a monolayer of the carbon black is  $104 \text{ } \mu\text{g BaP per mg carbon black}$ . The calculation assumes that no other organics are competing for the available surface area. This assumption is probably not strictly correct if isoeugenol is present because isoeugenol might also adsorb to CB. The highest concentration coating applied to the carbon black in this research was  $78 \text{ } \mu\text{g}/\text{mg}$ , for the Oct. 20 experiment. These calculations indicate that PAH were not likely to be present in multiple layers on the carbon black surface assuming no other organics were coadsorbed on the surface.

The concentration calculated for a monolayer of PAH is much higher than concentrations used in Table 2.5 for PAH adsorbed on model combustion particles which typically were in the  $75 - 500 \text{ } \mu\text{g per gram}$  range. The studies reported in Table 2.3 included no other associated organics, and therefore less than monolayer coverage of PAH was likely. The surface area calculated from the measured mass median diameter was  $3 \text{ m}^2/\text{g}$ , this is the external surface area for a spherical particle with a mass median diameter of  $12.5 \text{ } \mu\text{m}$ . The surface area obtained using BET adsorption isotherms measured the total surface area available for nitrogen gas adsorption. Typical carbon black may be characterized as micrometer size agglomerates of nanometer size particles (Goldberg, 1985). The discrepancy between the BET surface area and the external surface calculated for  $12.5 \text{ } \mu\text{m}$  carbon black particles is most likely due to available surface within the agglomerated particles.

As discussed later carbon black slowed the reactivity of PAH when the filters were exposed to light after slurry coating preparation (Table 4.4a). The stabilization of PAH reactivity may be due to the physical properties of the carbon black. The

mechanisms by which carbon black stabilizes PAHs to photolysis may be similar to those postulated by Korfmacher et al. (1980) for PAHs adsorbed on fly ash particles. The total surface area to which the PAH are adsorbed may be greater than the cross-section exposed and PAH may be shielded from the light by adsorption to inner pore surfaces of the carbon black agglomerates (Korfmacher et al., 1980). Carbon black also may be absorbing light which would be reflected back out through the organic layer (Behymer and Hites, 1988).

The stabilization of PAH reactivity could also be due to chemical properties of the carbon black (Nielsen et al., 1983). The chemical structures of the adsorption sites of particle-associated PAH contain surface groups such as carboxylic acids, phenolic hydroxyl groups, carbonyl groups, and quinones (Goldberg, 1985; Chang & Novakov, 1983; Smith et al., 1989). PAHs adsorbed to carbon black surfaces may be chemisorbed, the chemical properties of the PAH being altered by their adsorption to the surface (Eiceman, 1983; Natusch and Tomkins, 1978). These PAH may be unavailable for absorption of UV and excitation into the triplet state, or have shorter triplet excited state lifetimes, or are resistant to degradation by other normal pathways for degradation (Nielsen et al., 1983).

The stabilization of PAH due to adsorption on carbon black has been observed in an outdoor chamber experiment (Kamens et al., 1985). Particles slurry coated with fluoranthene, anthracene, pyrene, and fluorene concentrations of 50ng/mg-100ng/mg were injected into the chambers using a cyclonic device. Little if any decay of PAH concentration on the particles was observed in the presence of sunlight. PAH adsorbed on carbon black were found to be stable which contrasted the observed photoreactive behavior of PAH on wood combustion particles. The observed photoreactivity on real combustion particles indicates that the measured stability for PAH adsorbed on carbon black particle without organic co-adsorbates may only be relevant to fly ash carbon particles or particles from incinerators. Here PAHs probably are adsorbed directly on



to an elemental carbon surface for particles generated using high temperature combustion.

### 5.B Coating Technique

Development of a method to permit control over the amount and type of organic compounds adsorbed to the carbon black surface involved choosing an adsorption technique. A vapor phase deposition technique was developed by Korfmacher et al. (1979). However, the equipment required to perform this experiment was not available to us. In addition, due to the extreme toxicity of these compounds it was preferable to avoid placing large quantities of PAH in the gas phase. An alternative method of adsorbing the compounds from a liquid phase onto the carbon black particles was investigated. A Buchner funnel was used to suspend coated particles in an organic solvent above a 47mm filter, solvent drawn through the filter leaving particles distributed evenly on top of the filter (see Section 3A).

Developing the liquid dispersion technique required choosing a solvent, a transfer method, type of filter, and determining the concentration of organics to place in the liquid phase with the particles.

The solvents chosen were dichloromethane and pentane, which were good candidates due to their low boiling points of 40-41°C and 35-37°C respectively, and due to PAH solubility in them. PAHs are polarizable compounds which are more readily extractable by polar solvents than in nonpolar solvents (Grant and Higuchi, 1990). Selectivity in solubility for these polarizable compounds is due to the relative importance of the Debye interactions which are not as well understood as dispersion or London forces by which non polar molecules interact (Grant and Higuchi, 1990).

The goal of the initial coating experiment of January 8 was to determine in what amounts the organic constituents would be adsorbed on to the carbon black surface using the BFF technique. Recovery measurements were made, comparing the



concentration of PAH retained on the carbon black and filter to the concentration of the PAH in the coating solution applied. The results showed generally low recoveries for all of the PAH (Table 4.7). The lower molecular weight PAH (e.g., fluoranthene) were adsorbed by the carbon black very little, and only 1-10% of the PAH in the coating remained on the carbon black on the filter. The higher molecular weight PAH (e.g., benzo(a)pyrene) were more strongly adsorbed by the carbon black, with >20% recovery. The solvent used was dichloromethane. The effectiveness of the method used to transfer the coated particles is reflected in the observed recovery, in addition to the desired measure of adsorption capacity of the carbon black. The most efficient means identified to transfer the coated particles to the liquid phase was to scrape most of particles off the walls of the glass vial using a spatula (Section 3.A, Table 4.7).

Additional work was conducted to improve carbon black adsorption of the organic constituents by reducing the solubility of the PAH in the liquid phase. Recovery trials were performed using pentane or dichloromethane as the solvent, to determine which maximized PAH adsorption on carbon black. The technique used for transferring the coated particles was to use a spatula to transfer the majority of the particles to the liquid phase, then to sonicate and transfer any remaining particles from the walls of the glass vial (sonication method, Section 3A). The results of this experiment show that use of pentane as the liquid phase significantly increased the adsorption of PAH onto the carbon black surface (Table 4.8). The recovery of BaP was 54% in pentane and only 20% in dichloromethane. Thus, by reducing the affinity of the organic constituents for the solvent, greater affinity for the carbon black surface was promoted. The liquid phase may be chosen based on its ability to keep the PAH in contact with the carbon black surface. At high concentrations isoeugenol would separate out due to its low solubility in pentane, thus when higher concentrations of adsorbed isoeugenol were desired, it was necessary to use dichloromethane as the liquid phase.

Consideration was given to a variation of the BFF technique which would place the organic constituents and carbon black in the liquid phase separately (no transfer method, Section 3A) (Table 4.9). This method was considered to avoid loss of the PAHs incurred when precoating them in a vial. Placing the organic coating solution directly in the liquid phase, and then adding the carbon black required that the coating compounds adsorb to the carbon black from solution. Once the particles and coating were evenly mixed the liquid phase was drawn through the filter, evenly dispersing the particles on top of the filter. Recovery trials using the sonication method and the no transfer method were performed (Section 3.A). The no transfer method gave lower recoveries of the PAHs (Table 4.9). The possibility exists for the PAH to diffuse and adsorb to the glass walls of the funnel in addition to the carbon black, which would contribute to loss of PAH. More carbon particles were lost during transfer of uncoated carbon black from the vial to the Büchner funnel than were lost using the no precoating transfer method. The particles coated with isoeugenol and PAH were observed to be easier to physically remove from the glass surface than carbon black particles. Dichloromethane was used to transfer both the coated and the uncoated carbon black from the vial to the Büchner funnel. Lower recoveries which were observed in the no precoating transfer method may be due to the lower particle surface area available for the PAH to adsorb to when particles are lost. An alternative reason for higher recoveries observed with precoating the particles may be that the coating adsorbed to the carbon black prior to the particles being dispersed in the liquid phase remain adsorbed, and that an adsorption equilibrium was not established in the liquid phase. The method of precoating in a vial prior to particle dispersion in the liquid phase was resumed as the best way to coat and transfer particles using the Büchner funnel technique.

A low adsorbing filter material was chosen to support the coated carbon black particles on the basis of results obtained by Behymer and Hites, that photodegradation

rates of adsorbed PAH are influenced by surface characteristics (Behymer and Hites, 1985). The method was devised to ensure that the photodegradation rates observed were for PAH adsorbed on the carbon black and not on the filter surface. Teflon Zefluor filters were chosen to avoid adsorption of the organic constituents from the liquid phase or the carbon black to the filter surface. The reported filter surface area for a 2  $\mu$ m Zefluor filter is 26 ( $\text{m}^2$  surface area)/( $\text{m}^2$  exposed filter area) and this value is less than the 126 ( $\text{m}^2$  of surface area)/ ( $\text{m}^2$  exposed filter area ) for Pallflex QAOT quartz filters (Turpin, 1986).

The relative adsorption of the PAH by the filter only, compared to adsorption by the carbon black and the filter is shown in Table 4.10. The results of this experiment justified the extra expense of the Teflon filter compared to quartz fiber filters, as less than 1% of all the organic constituents were recovered or adsorbed by the filter and greater than 20% adsorbed by the carbon black (Figure 5.1). The relative adsorption of PAH by carbon black versus the filter is also dependent upon the concentration of PAH in the liquid phase, as discussed below.

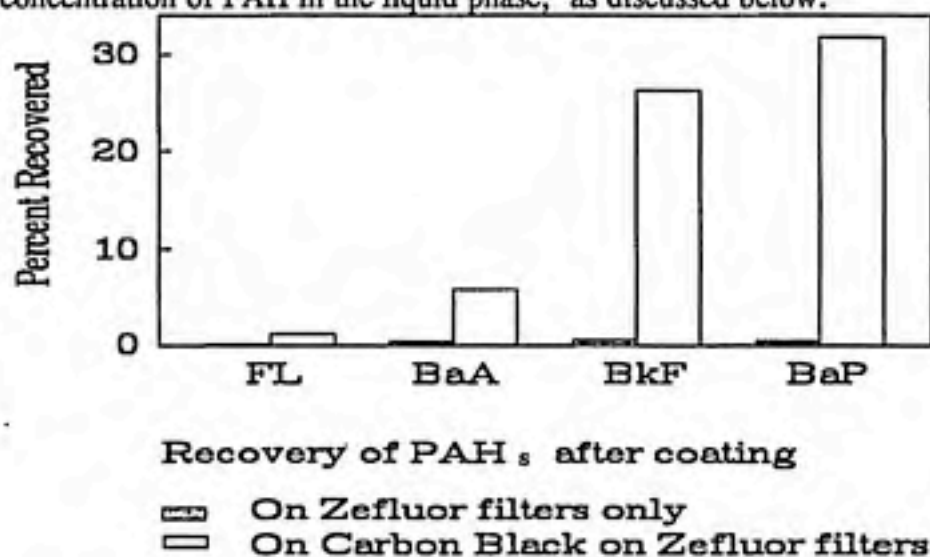


Figure 5.1. Verification that organics are adsorbed to the carbon black surface and not on the Zefluor filters

Concentration of the organics may also influence the particle composition, in addition to the distribution of the constituents between the particle and the filter. The concentrations of constituents used in the organic layer for adsorption by the carbon black were increased between phase V and phase VII experiments in an effort to obtain adsorbed concentrations similar to those observed on combustion particles, which are 50 - 200ng/mg (see Table 5.1).

Table 5.1 Table of Standard Concentrations

Name of Standard	Standard #1	Standard #2	Standard #3
Date Prepared	September 13, 1991	June 19, 1992	August 26, 1992
Compound	Concentration (ng/ul)	Concentration (ng/ul)	Concentration (ng/ul)
Fluoranthene (Fl)	200	400	1600
Benz(a)anthracene (BaA)	40	80	320
Benzo(k)fluoranthene (BkF)	25	60	240
Benzo(a)pyrene (BaP)	25	60	240

To reaffirm that these compounds were being adsorbed by the carbon black, and not retained by the filter, additional coating recovery experiments were performed. The analysis of the results led to the conclusion that the PAH concentrations in the stock solution were too high. The carbon black surface is only able to adsorb a certain amount of organics from solution. As the liquid phase concentration increases beyond the concentration needed to obtain equilibrium between adsorption on the surface and concentration in solution, a higher percentage of the organic constituents is drawn through the filter. As the percentage drawn through the filter increases, the amount retained by the filter relative to that absorbed by the carbon black increases as well.

Four percent of the BaP in solution was recovered from the carbon black and filter, 1% was retained by the filter only and the remaining PAH passed unadsorbed to the flask below (Table 4.19). Lower concentrations of isoeugenol should be used to avoid placing the organic constituents on the filter in addition to the carbon black. Despite the high concentrations of PAH and the low recovery, 80% of the adsorbed PAH were on the carbon black and only 20% on the filter. While PAH concentrations should be sufficiently high to observe reactivity differences, there is a limit as to how much can be put on the particles without causing large amounts of the PAH to adsorb on the filters. The observation that eighty percent of the PAH remained adsorbed to the carbon black surface indicates that the observed photoreactivity will be relevant to combustion particles, and not simply the photoreactivity of PAH adsorbed on filter material.

Fluorescent microscope examination of the filters led to insights about the distribution of the PAHs in hexadecane versus isoeugenol. Hexadecane and isoeugenol were the two compounds which were initially chosen to represent constituents of the organic layer on combustion particles. A primary concern was whether or not the isoeugenol was in contact with the PAH on the surface of the particle. The pictures indicated where the PAH was in the medium as it fluoresced with a green color when irradiated by light from the microscope's mercury lamp. When PAH were placed in solution with hexadecane and isoeugenol, a predominance of PAH were observed via fluorescence in the isoeugenol phase compared to the hexadecane phase. The microscope pictures also clearly showed that isoeugenol and hexadecane were immiscible. A coating solution of PAH was directly applied to a filter containing carbon black (slurry coating technique, Section 3A) and then observed under the microscope. In the photographs one could observe PAH crystals outlining the edges of the carbon black, although some fluorescence on the filter separate from the carbon



black was observed. PAH on the filter not adsorbed to carbon black were not as visible in photographs of particles prepared using the BFF technique (Section 3.A).

SEM Photographs illustrated that the carbon black particles were evenly distributed on the filter for particles with 1% adsorbed PAH and 10% adsorbed isoeugenol (Figure 5.2). When the isoeugenol concentration was increased to 30% of the particle mass the SEM photographs may be described as showing particles engulfed by a layer of isoeugenol on the filter surface (Figure 5.3). On the basis of these photographs the isoeugenol concentrations of the coating were reduced in subsequent experiments (after Aug 19) to keep adsorption on the carbon black of isoeugenol less than 10% of the particle mass. Based on these studies the BFF technique of preparing particles by adsorbing organic constituents from a liquid phase onto a solid carbon black surface was demonstrated to be a reproducible adsorption technique for use in studying heterogeneous PAH photodegradation rates.

### 5.C Dark Reactivity

To determine whether photolysis was primarily responsible for PAH reactivity on heterogeneous surfaces the extent of reactivity by dark thermal reaction or evaporation must be characterized. Results of slurry coating experiments of PAH adsorbed on filters indicate that PAH are stable in the dark but reactive when exposed to light in the turntable photoreactor (Table 4.3a, Table 4.4a). A similar experiment was carried out for PAH adsorbed on the filter surface (Table 4.1) This reactivity on filter media was similar to that observed in solution (McDow et al., 1991), indicating that PAH are not stabilized significantly by the filter surface.

The rate of PAH reaction in the dark for PAH adsorbed on carbon black surface was compared to that measured for PAH adsorbed on filter media in slurry coated experiments performed in phase 2. The presence of the carbon black appeared to enhance the reactivity of the PAH in the dark. The observed half-life for BaP adsorbed



on carbon black was 2.3 hours. The half-life for BaP adsorbed on filters was much longer than the duration of the experiment (Table 4.3a). The quality of the data in Table 4.3a obtained for PAH adsorbed on the carbon black was questionable due to poor extraction recoveries of the PAH from the carbon black. On carbon black PAH was concluded to be more stable in the dark than when exposed to light. As discussed below, the observed dark reaction rate much was still slower (BaP half-life = 2.28 hr, Table 4.3a) than the reaction rate observed when filters are exposed to light (BaP half-life = .81 hr, Table 4.4a) for the slurry coated carbon black particles. PAH adsorbed on carbon black with and without isoeugenol using the BFF technique exhibited stability in the dark relative to the light (Table 4.11, Figure 5.4). The half-life for BaP adsorbed on carbon black was both with and without isoeugenol on carbon black was much greater than the experiment duration (Table 4.11). On the basis of these experiments degradation in the reactor was attributed to being driven by photochemical reactions and not by thermal reactions influenced by either carbon black surface or filter surface.

#### 5.D Adsorbed organic concentration

Isoeugenol, a compound in wood combustion particles, has been shown to significantly enhance PAH photodegradation when present in solution with PAH (McDow et al., 1992). The work of Hawthorne et al. (1988) suggests that 20 - 30% of wood soot particle mass is composed of methoxyphenolic compounds. Isoeugenol was used to represent this class of compounds with a target concentration of 10% of the total carbon black particle mass. Hexadecane was chosen initially to represent the aliphatic portion found in combustion aerosols, and its target concentration for the model particle was 40% by mass. PAHs were represented by fluoranthene, benz(a)anthracene, benzo(k)fluoranthene, and benzo(a)pyrene and contributed 1% to the mass of the particle. When the BFF method was used there were several occasions

when the adsorbed organic concentrations were lower than amounts found on real combustion particles, as indicated by the percentage of PAH mass adsorbed on the carbon black in Table 5.2. These problems may be due to poor extraction from the carbon black surface. Attempts were made to influence reactivity by changing the adsorbed organic concentrations, but other experimental factors such as organic distribution between the liquid or solid phase, or exposure conditions may have been more influential.

Table 5.2				
Concentration of adsorbed organics for Photodegradation experiments using BFT				
Date of Exp.	Standard #; Conc. of BaP applied (ng/ul)	% PAH adsorbed to CB	% Isoeugenol adsorbed to CB	Experimental Modifications
March 26	#1 ; 25	.32	.9	
April 20	#1 ; 25	.24	2.6	Increased [Isoeugenol].
May 14	#1 ; 25	.24	2.6	Short Time Interval
May 24	#1 ; 25	.44	5.2	Triplicate samples, iso. only
June 19	#2 ; 60	.94	3.5	Duplicate Samples
July 18	#2 ; 60	1.2	43	Increased [isoeugenol]
Aug. 11	#2 ; 60	.087	22	Borosilicate well
Aug. 28	#3 ; 240	1.08	16	light filters
Sept. 9	#3 ; 240	1.48	10	light filters

When particles were coated and exposed to light using the BFF method, photodegradation was observed, but it occurred to a much lower extent than that

observed in the preliminary slurry coated experiments. The half-life measured for BaP using the Büchner funnel filtration method was 4.6 hours (Table 4.12). PAH reacted quickly when coated on carbon black using a slurry coating method. The half-life was 0.23 hour for BaP (Table 4.6a). A difference in PAH concentration between the two experiments is one possible cause since the PAH concentration for the slurry coating method was 7.2%, and for the Büchner funnel filtration method was 0.32%. PAH concentrations on combustion particles generally range from 0.5 to 5% of the total particle mass. A possible explanation is that PAH at lower particle concentrations may be bound to the particle surface as a monolayer and consequently unavailable for reaction. The calculation of the amount of PAH which may be adsorbed by a  $95\text{m}^2/\text{g}$  surface area particle indicated that the range of PAH concentrations used from 0.32% PAH to 10% PAH by weight concentration would be much less than monolayer amounts (Section 5.A). As the concentration is increased, multiple layers may form such that PAH are surrounded by other PAH instead of being adsorbed directly to the carbon black. The  $46 - 78\text{ }\mu\text{g}/\text{mg}$  PAH concentrations (representing of 4.6 to 7.8% of the particle mass) used in the slurry coating technique experiments may not have formed multiple layers but may coat the filter in addition to the carbon black. Evidence for PAH adsorption to the filter in addition to the carbon black as a result of slurry coating was observed in the fluorescent microscopy photographs. Similar adsorption of PAH to the filter in addition to the carbon black surface was not observed for filters prepared using the Büchner funnel filtration technique. The results may be interpreted as a reflection of the fact that when PAH are primarily adsorbed to carbon black they are stabilized to photochemical reactivity. In contrast when PAH are surrounded by other PAH or are adsorbed to filter media they are more photoreactive than if adsorbed to carbon black.

A difference in PAH photoreactivity on the carbon black particles due to isoeugenol's presence was not observed using the slurry coating technique. Only

fluoranthene disappeared faster in the presence of isoeugenol (Table 4.6a). The significance of the observations was questioned due to the inability to determine or control the distribution of PAH and isoeugenol adsorption on the carbon black surface and the filter using the slurry coating method. The results were puzzling because the previous experiments indicated that the PAH were adsorbed to the filter as well as the carbon black when the slurry coating technique is used. If this is the case then when isoeugenol is added it should be coadsorbed with the PAH on both the filter and the carbon black, and enhanced photodegradation should have been observed. It is possible that PAH and isoeugenol are not distributed uniformly on the carbon black surface. The higher molecular weight compounds such as BaP and BkF may be strongly adsorbed to the carbon black while the lower molecular weight compounds isoeugenol, Fl, and BaA are absorbed more evenly by the carbon black and filter surface. Enhancement of PAH photodegradation may be dependent on the spatial proximity of PAH to the nearest neighboring isoeugenol molecule. Fluoranthene, which has an intermediate affinity for the carbon black surface between that of BaP or isoeugenol, may be more concentrated on the filter than the particle surface relative to the other PAH. Isoeugenol may not differentiate between the particle and filter surfaces and may be relatively more concentrated on the filter surface because of its high volatility. Carbon black stabilization of the higher molecular weight compounds may suppress any reactivity enhancements due to the presence of isoeugenol. Observation that only fluoranthene's reactivity was enhanced may indicate that it is more likely to adsorb near isoeugenol, or that a smaller fraction of fluoranthene than of benz(a)anthracene or benzo(a)pyrene is adsorbed on to the carbon black making the stabilizing effect of CB less for fluoranthene. Alternatively, the results could be explained by evaporation of fluoranthene. The results of this experiment led to development of the BFF technique to ensure the proper physical environment, (adsorption to the carbon black, not the filter) for the PAH in addition to the chemical composition of the organic layer. A



factor which ultimately proved important to the observation of isoeugenol's influence on PAH photodegradation was the UV light characteristics, as discussed in Section 5G.

For the August 11 experiment the data for BaP on particles coated only with PAH were highly variable, either due to poor extraction recovery or bad stock solution (Table 4.18a). The BaP concentration adsorbed by the carbon black was very low (.09%), and may have been unextractable from the surface (Eiceman and Vandiver, 1983). BaP concentrations found on the filters with isoeugenol adsorbed to the carbon black were consistent. This indicates that BaP may be lost due to irreversible adsorption onto the surface when isoeugenol is a co-constituent of the organic layer. Preparation of a new stock solution of higher concentration resulted in two successful subsequent experiments which had higher PAH concentrations adsorbed to the carbon black surface (August 28 & Sept. 9).

#### 5.E Variability in filter samples.

The particles were exposed to light using a turntable reactor which permitted all of the filters to be exposed to the same amount of light. A high amount of variability in the data of the April 20, and May 14 experiments was observed as discussed below. An experiment was performed on May 24 to measure the reproducibility for triplicate filters with the same concentration of PAH and isoeugenol adsorbed on the carbon black particles, exposed to light for the same intervals of time (see Table 4.15). This experiment addressed the problem of whether or not particles were falling off the filters during the time that they were rotated around the UV lamp. The random loss of particles from the filters during exposure would explain the observed variability in the data for the previous experiments. Table 4.15a indicates that this is not the case because reproducibility is still good after .75 hour. The use of the BFF technique to determine PAH reactivity on organically coated particles was continued.

As mentioned above the data obtained for the April 20th and May 14th experiments were extremely variable. The problems were attributed to either poor extraction techniques, degraded stock solution, poor miscibility in the solvents used, or to particle loss during exposure in the turntable. BaA, BaP, and BkF were not consistently detected on the filters (Table 4.13). The results indicate that fluoranthene loss is enhanced when isoeugenol is present (Table 4.13, Table 4.14). The photodegradation rate of BkF may be slightly enhanced, but the scatter in the data is larger than any observable trend. Again, the characteristics of the UV light were determined ultimately to be important to the behavior of the PAH and isoeugenol adsorbed to carbon black for these experiments as discussed in Section 5G. The May 24 reproducibility experiment illustrated that particles were not being lost during exposure in the turntable. Future experiments were performed using duplicate filter samples for each exposure time and condition. An example of the variability observed using this procedure is shown in Figure 5.5.

## 5.F Product Characterization

Phase VI was directed towards determining what was happening to the PAH as they were degrading. The aim was to characterize products, under the possibility that PAH would degrade to unique products when isoeugenol was present. A portion of a typical total ion chromatogram of the major compounds identified after irradiation is shown in Figure 5.6. The only PAH photodegradation product characterized was BaA 7,12-dione (Figure 4.2), which was generally present in concentrations which were too low to observe on the total ion chromatogram, but which could be observed in the selected ion chromatogram of ion 258 (Figure 5.7). BaA-7,12-dione was identified by comparison to its NBS Library spectrum (Figure 5.8). BaA-7,12-dione concentration increased with irradiation time (Figure 5.9). Two products of isoeugenol degradation, dehydrodiiisoeugenol and vanillin, were also observed, but their concentrations



appeared to decrease with irradiation time (Figure 5.9). Vanillin and dehydrodiisoeugenol were identified by spectral matching to NBS library spectra (Figure 5.10, Figure 5.11). Both of these compounds are known photodegradation products of isoeugenol (Eskins et al. 1972, Eskins, 1979). Recent experiments in solution suggest that the presence of vanillin strongly accelerates PAH photodegradation (McDow and Kamens, 1992). Many of the peaks were unmatchable to spectra available in the literature. The fragmentation patterns were not characteristic of expected PAH derivatives such as hydroxy or dihydroxy derivatives, ketones, carboxaldehydes, dicarboxaldehydes, other PAH quinones, and dicarboxylic acid anhydrides (Schuetzle et al., 1981; König, 1983). Many of these known PAH derivatives may oxidize during the analysis, may not elute from the GC column due to their thermal instability, or may react with the column substrate. Their concentrations also may be below the detection limit.

The use of hexadecane was discontinued due to the abundance of unidentified peaks in the GCMS chromatogram which were obtained in the analysis of extracts from the June 19 experiment. The goal was to simplify the number of reactants involved in PAH photodegradation on the particle surface, and to reduce the number of products formed.

#### **5.G Exposure to wavelengths below 290 nm**

It was determined that many of the experiments were performed using an exposure of UV wavelengths below 290nm. An assumption had been made that the immersion well was made of borosilicate material, which functions as a light filter by adsorbing wavelengths below 290nm. Quartz immersion wells do not filter out light below 290nm; therefore samples exposed using the quartz immersion well received wavelengths which are not atmospherically relevant (see Figure 3.3). The absorption spectrum for PAHs is very strong in the region below 290nm, therefore alternate

photodegradation pathways were likely. These degradation pathways, if stronger than the photodegradation mechanisms active due to wavelengths above 300nm, might result in no observable effect due to the presence of isoeugenol. This allowed evaluation of the importance of selection of UV light characteristics for the results to be atmospherically relevant. It is assumed that the quartz immersion well was used for experiments Nov. 28, 1991 through July 18, 1992.

### 5.H Atmospherically significant wavelengths

The most important result obtained using this technique was that the measured BaP photodegradation rate was enhanced due to the presence of isoeugenol in the organic layer adsorbed on the carbon black (Phase VII). The difference in the measured rates was statistically significant for BaP adsorbed on carbon black versus BaP and isoeugenol adsorbed on carbon black (Table 4.21). The results obtained are relevant to real combustion particles because the developed method models physical and chemical conditions for particle associated PAH in the atmosphere.

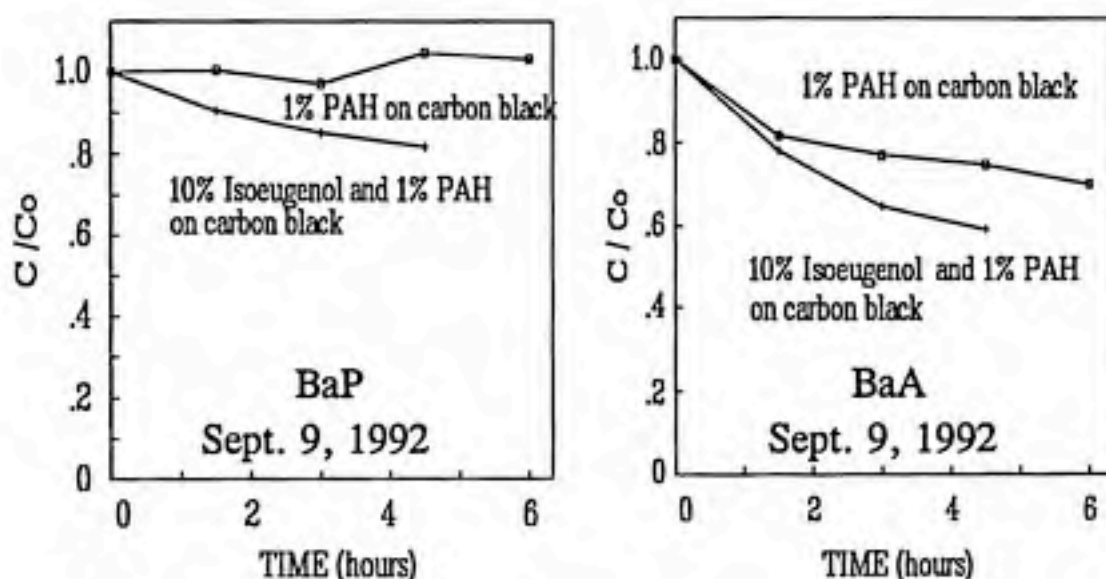


Figure 5.12: BaP and BaA photodegradation rates observed with and without isoeugenol coadsorbed on carbon black.

The greatest differences in PAH photodegradation rate due to isoeugenol were observed when optical filters were used to isolate the 366 nm mercury line (Tables 4.20 & 4.21, Figure 5.12, Figure 5.13, Figure 5.14). This was probably because the light was less intense and because the more energetic wavebands were filtered out, so that the reaction was slow enough to follow over several time intervals. The rates of photodegradation in both experiments were tested for parallelism (Kleinbaum et al., 1988) by comparing the slopes from the regressions of  $\ln(C/C_0)$  vs. time for PAH adsorbed on carbon black with and without isoeugenol. In spite of what look like similar rates in the presence and absence of isoeugenol, the hypothesis of parallelism was rejected for both BaA ( $p < .01$ ) and BaP ( $p < .05$ ) for the September 9 experiment indicating that there is a statistically significant difference between the rates (Figure 5.13a&b and 5.14a&b; Table 5.3 and 5.4). In the August 28 experiment significance was borderline for BaP ( $.05 < p < .10$ ) and the hypothesis of parallelism could not be rejected for BaA. These results are supported by results of a third experiment, in which light was filtered with a borosilicate well (Table 4.18, Figure 5.15).

The light filters used in these experiments removed all but the 366nm wavelength, thereby reducing the light intensity by 90% (Tables 4.20 & 4.21). The purpose of this was to slow down the reaction, and use UV light relevant to atmospheric exposures so that the rate of the fast initial degradation pathway observed in previous experiments could be measured. An experiment of 3hr duration, with 0.75 hour intervals was performed to compare whether isoeugenol enhanced PAH photodegradation on the particles using 366nm wavelength exposure. The results indicated that BaP was reacting faster in the presence of isoeugenol, but a significant amount remained on the carbon black after 3hr (Table 4.20). A second experiment was 6hr in duration with 1.5hr sampling intervals, to investigate the photoreactivity of adsorbed PAH exposed to light for longer times. BaP again exhibited the enhanced

reactivity in the presence of isoeugenol, with much of the BaP still remaining on the carbon black after 4.5 hours (Table 4.21).

The first experiment performed using a new borosilicate well indicated that BaP photodegraded at an enhanced rate when isoeugenol was present in the organic layer of the particles (Exp 8/11). However, the results of this experiment were not conclusive for two reasons. First, the reaction took place too rapidly, and second, the PAH concentration of .09% of the particle mass was too low (Table 4.18a). The mass percentage of PAH remaining on the carbon black at 1.5 hr was similar to that observed after the first 0.5 hr exposure, indicating that the PAHs reacted initially very fast, and then were stable over the next hour of UV exposure (Table 4.18b).

Figure 5.12 illustrates the trends in the data obtained for the behavior of adsorbed BaP when exposed to 366 nm light in the Sept. 9 experiment. The difference between the slopes obtained from the averaged concentrations for two filters at each exposure time and condition were statistically significant for the curves illustrated in Figure 5.12. To test the significance of the change in rate due to isoeugenol the log of the concentration at time =  $t$  divided by the initial concentration is plotted against time =  $t$ . To compare the two straight lines, a single regression equation 5.1 containing dummy variables to distinguish between the groups being compared (with and without isoeugenol) was used.

$$\ln(C/C_0) = \beta_1 \cdot T + \beta_2 \cdot I \cdot T \quad \text{eq. 5.1}$$

$C$  is the concentration at time =  $t$ ,  $C_0$  is the concentration at zero time,  $I = 0$  for with no isoeugenol coadsorbed with the PAH,  $I = 1$  for with isoeugenol coadsorbed with PAH on carbon black,  $\beta_1, \beta_2$  are the slopes determined from the fit of the regression equation and express the rate of PAH photodegradation. The independent variable is zero at time = 0 ( $C = C_0$ ), therefore the intercept was fixed at zero in the regression equation. The goal was to determine if the rate of PAH degradation when isoeugenol was present was different than in its absence. If there was no influence due to the

presence of isoeugenol the rates would be the same, and therefore the lines parallel and coincident, therefore  $\beta_2 = 0$ . The null hypothesis of no influence on the rate of photodegradation due to isoeugenol was tested using SYSTAT, a statistical package for the IBM PC (Wilkinson, 1986). A multivariate general linear hypothesis (MGLH) was used to test the model equation 5.1. The 90% confidence intervals and the data fitted with a linear regression line are illustrated in figure 5.16a for BaP with no isoeugenol, figure 5.16b for BaP with isoeugenol, figure 5.17a for BaA with no isoeugenol, figure 5.17b for BaA with isoeugenol. Table 5.3 gives the SYSTAT MGLH regression results for BaP which supports the rejection of the hypothesis that there is no influence due to isoeugenol with a p-value less than .05, and Table 5.4 contains the results for BaA with a p-value less than .01. The BaP concentration adsorbed on carbon black was observed to be stable, or remain fairly constant. BaP coadsorbed with isoeugenol on carbon black was observed to undergo photodegradation, degrading 20% after 4.5 hours of exposure. These results indicated that the composition of the organic layer was an important determinant of PAH photoreactivity on carbon black. The results obtained are likely to be applicable to real combustion particles due to the efforts made to emulate their physical and chemical properties in the atmosphere.



Zefluor Filter Only



Zefluor Filter + 1.0 mg Carbon Black

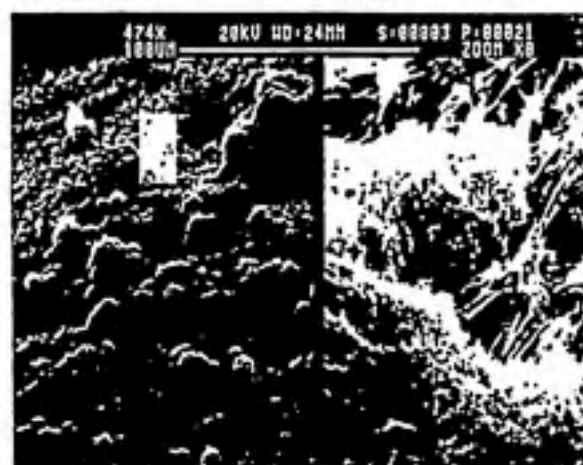
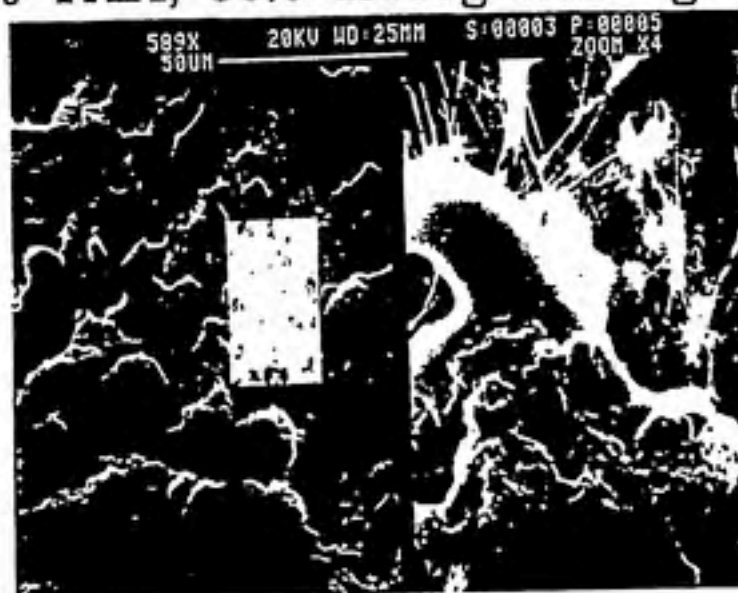
Zefluor Filter + 1.0 mg Carbon Black  
with 1% PAH, 10% Ioeugenol Organic Layer

Figure 5.2. Scanning Electron Microscopy Photographs



Zefluor Filter + 1.0 mg Carbon Black  
with 1% PAH, 30% Ioeugenol Organic Layer



Zefluor Filter + 1.0 mg Carbon Black  
with 1% PAH, 30% Ioeugenol Organic Layer

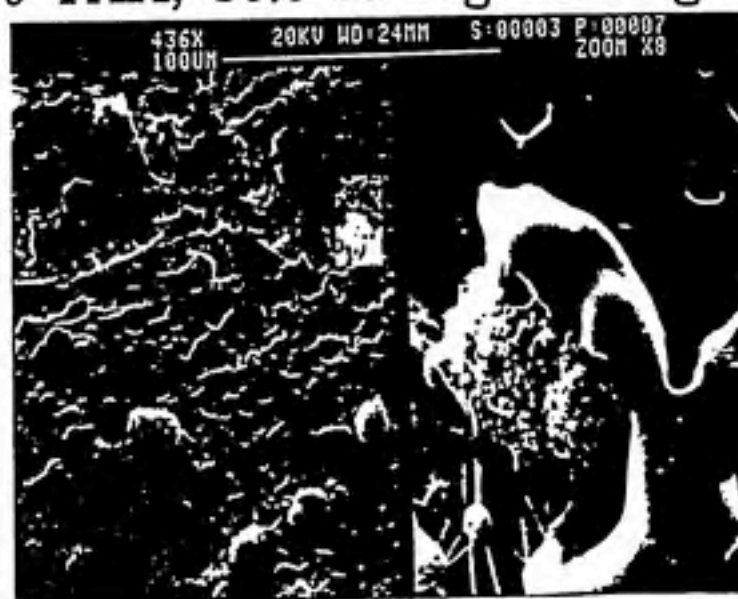


Figure 5.3. Scanning Electron Microscopy Photographs

March 18, 1992

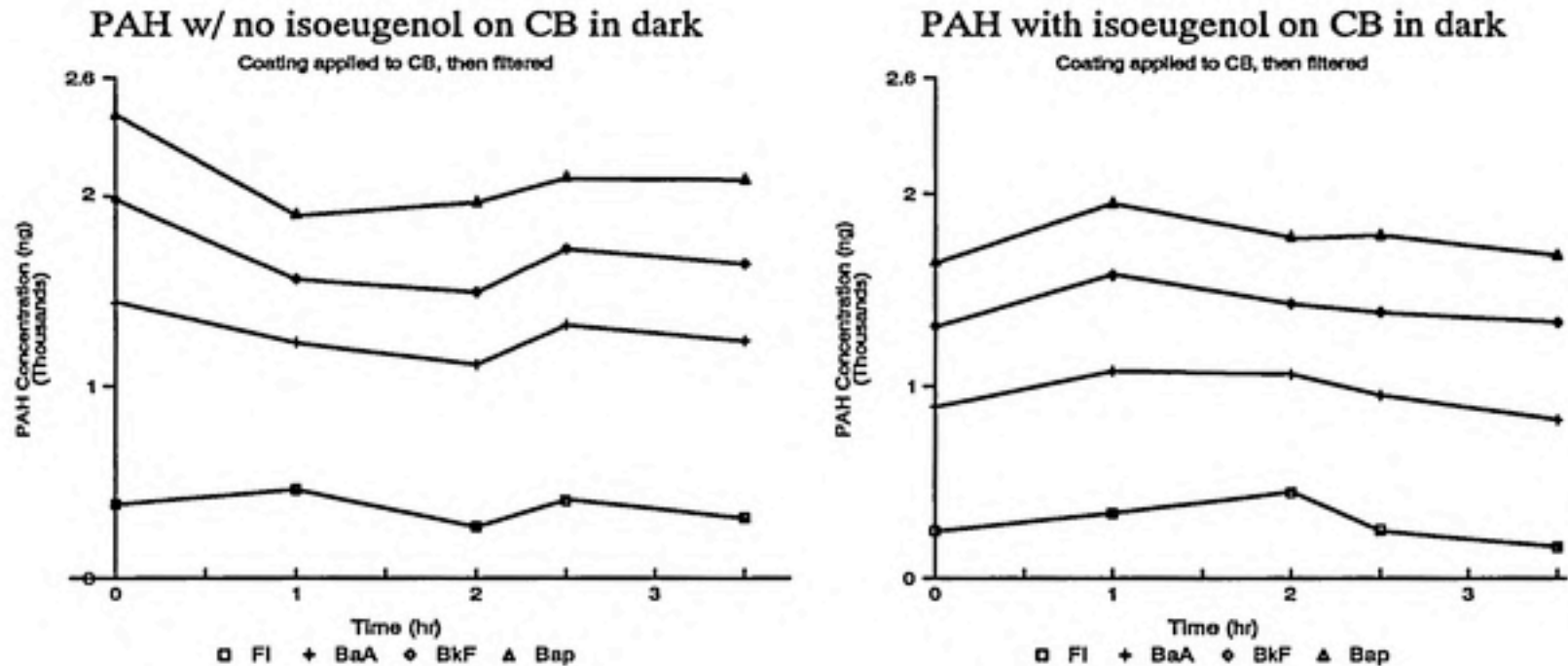


Figure 5.4 PAH stability in the dark adsorbed on carbon black with and without isoeugenol

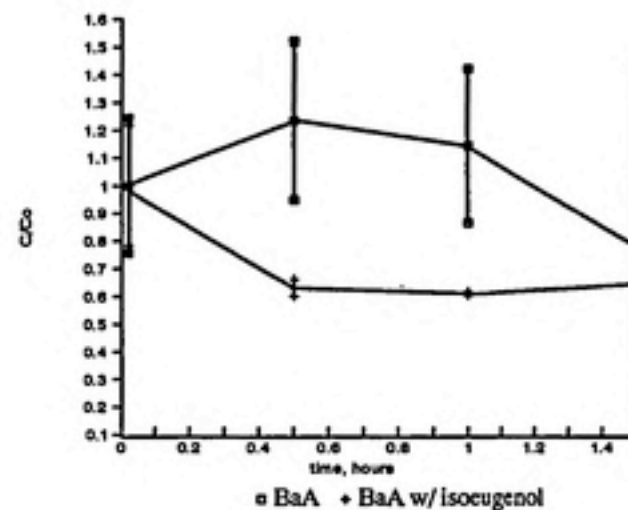
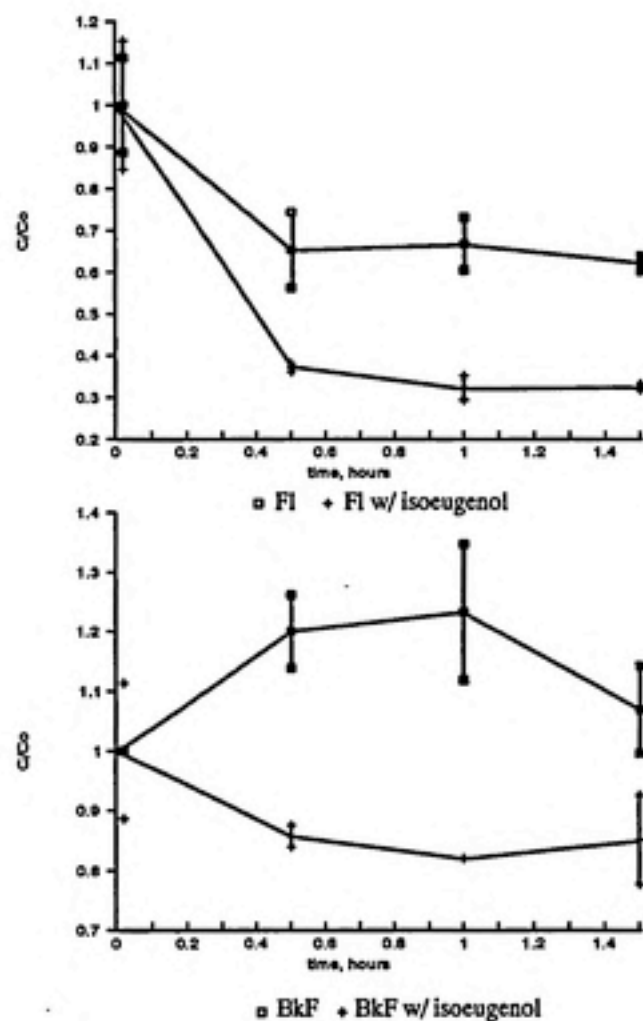


Figure 5.5. PAH Photodegradation on carbon black; range and mean of duplicates is shown.

File: D:\CHEMPC\DATA\622#7.D  
Operator: liz  
Date Acquired: 22 Jun 92 4:20 pm  
Method File: PAH\_SCAN.M  
Sample Name: #7 in 200ul acn + 200ul mecl2  
Misc Info: inj 1ul  
ALS vial: 1

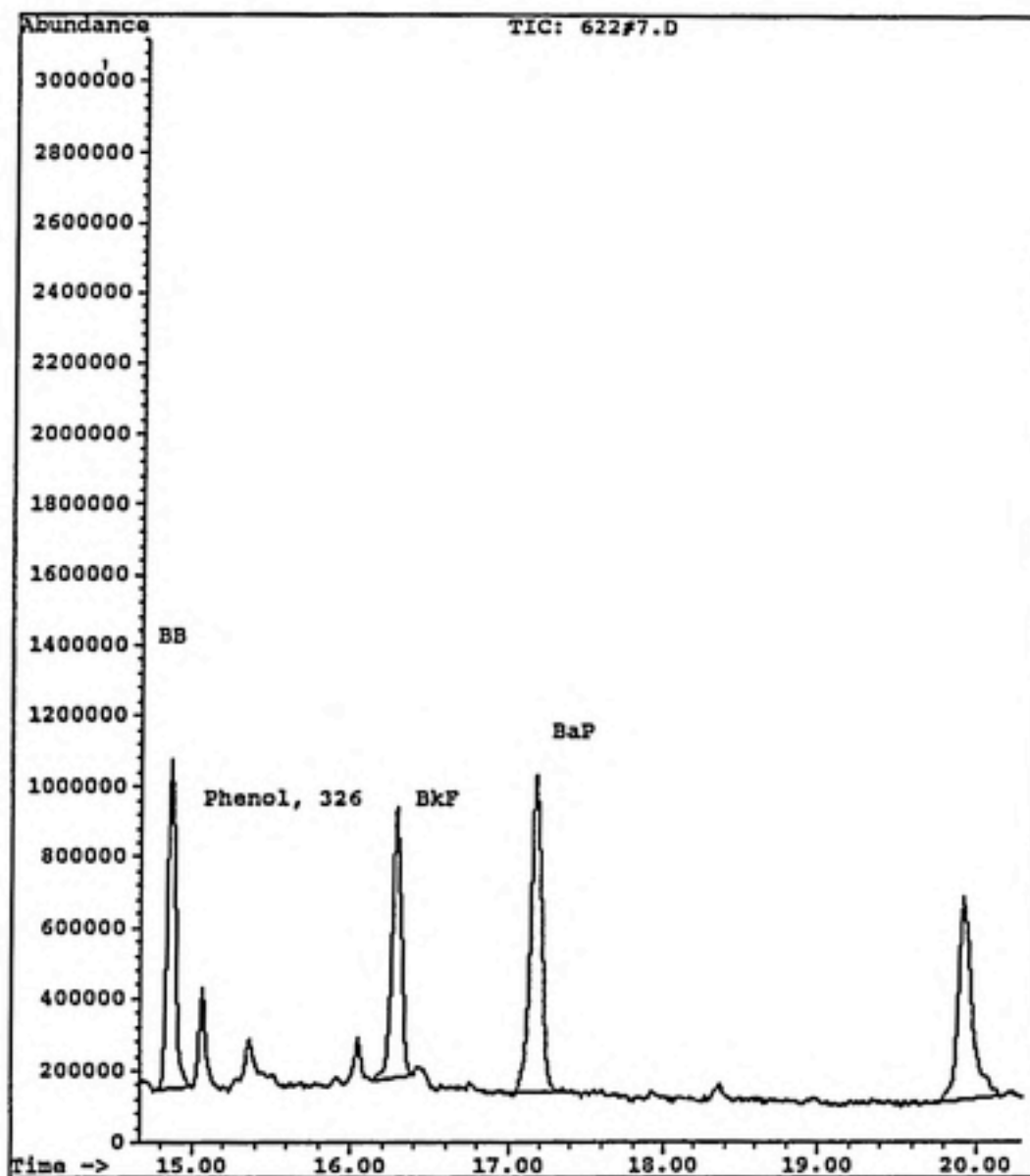


Figure 5.6. Partial GCMS Chromatograph of Compounds

File: D:\CHEMPC\DATA\622#13.D  
Operator: liz  
Date Acquired: 22 Jun 92 10:38 pm  
Method File: PAH\_SCAN.M  
Sample Name: #13 in 200ul acn + 200ul mecl2  
Misc Info: inj 1ul  
ALS vial: 1

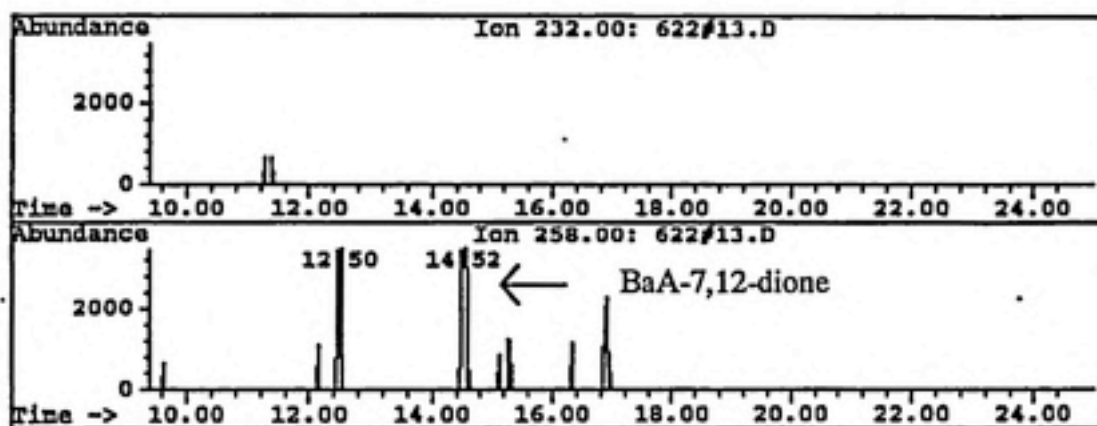


Figure 5.7. Selected Ion Chromatogram of Ion 258

Library Searched : D:\DATABASE\NBS49K.L  
Quality : 90  
ID : Benz[a]anthracene-7,12-dione (8CI9CI)

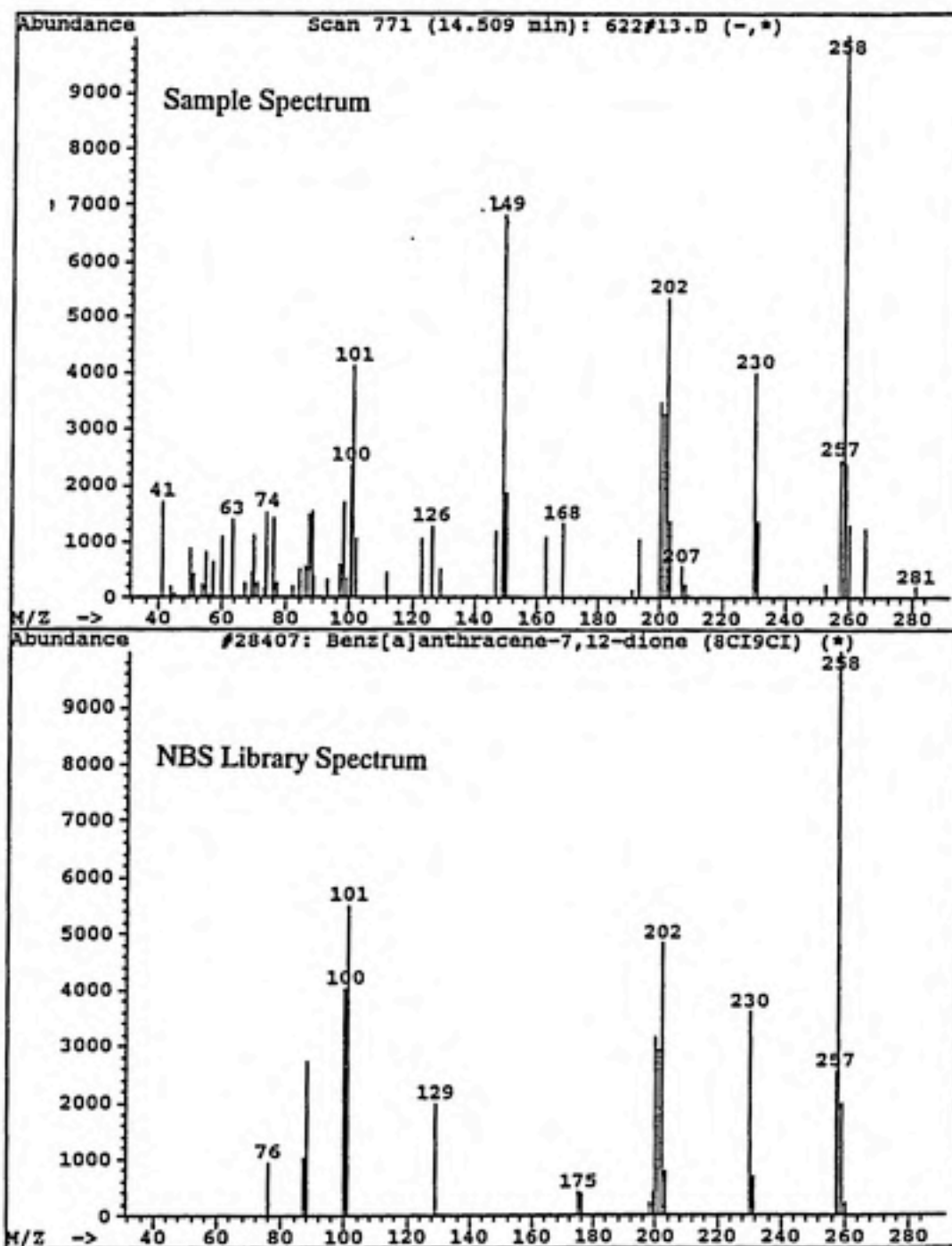
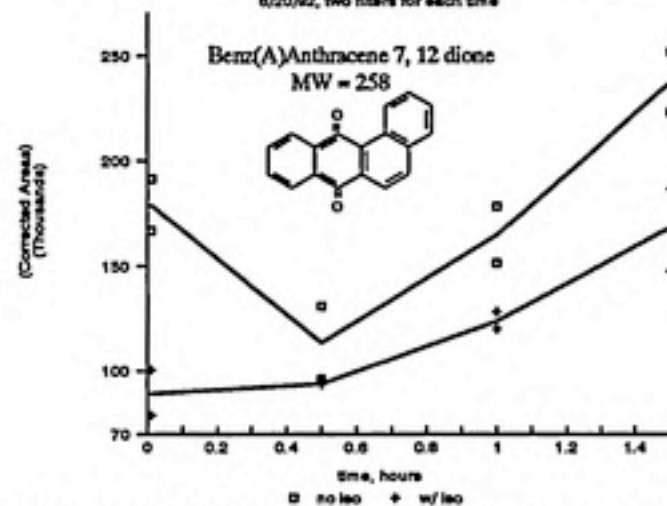


Figure 5.8. Match of unknown M.W. 258 with NBS Library Spectrum



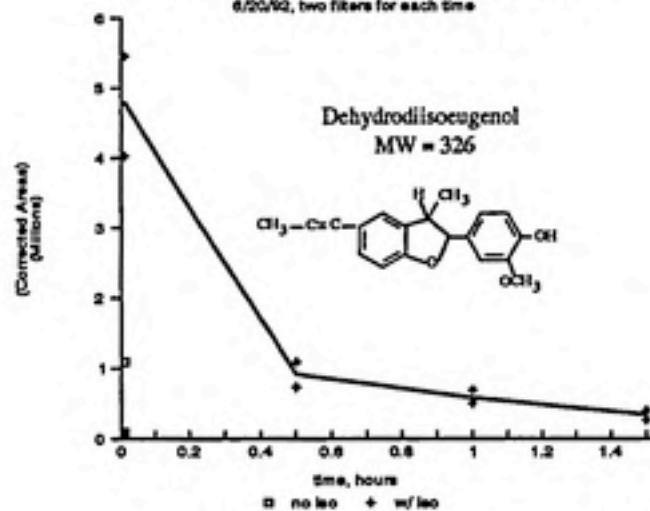
### Unknown 258 formed on CB w/ PAH in TT

6/20/92, two filters for each time



### Unknown 326 on CB w/ PAH in TT

6/20/92, two filters for each time



### Unknown 152 on CB w/ PAH in TT

6/20/92, two filters for each time

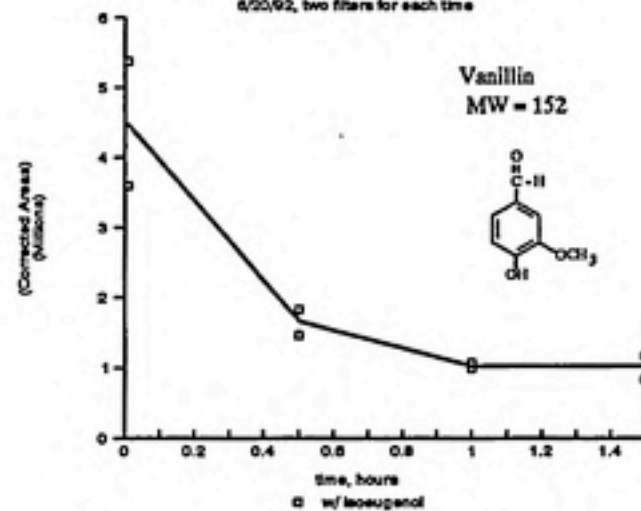


Figure 5.9 Products of PAH and isoeugenol degradation

Quality : 91  
ID : Phenol, 4-[(2,3-dihydro-7-methoxy-3-methyl-5-(1-propenyl)]

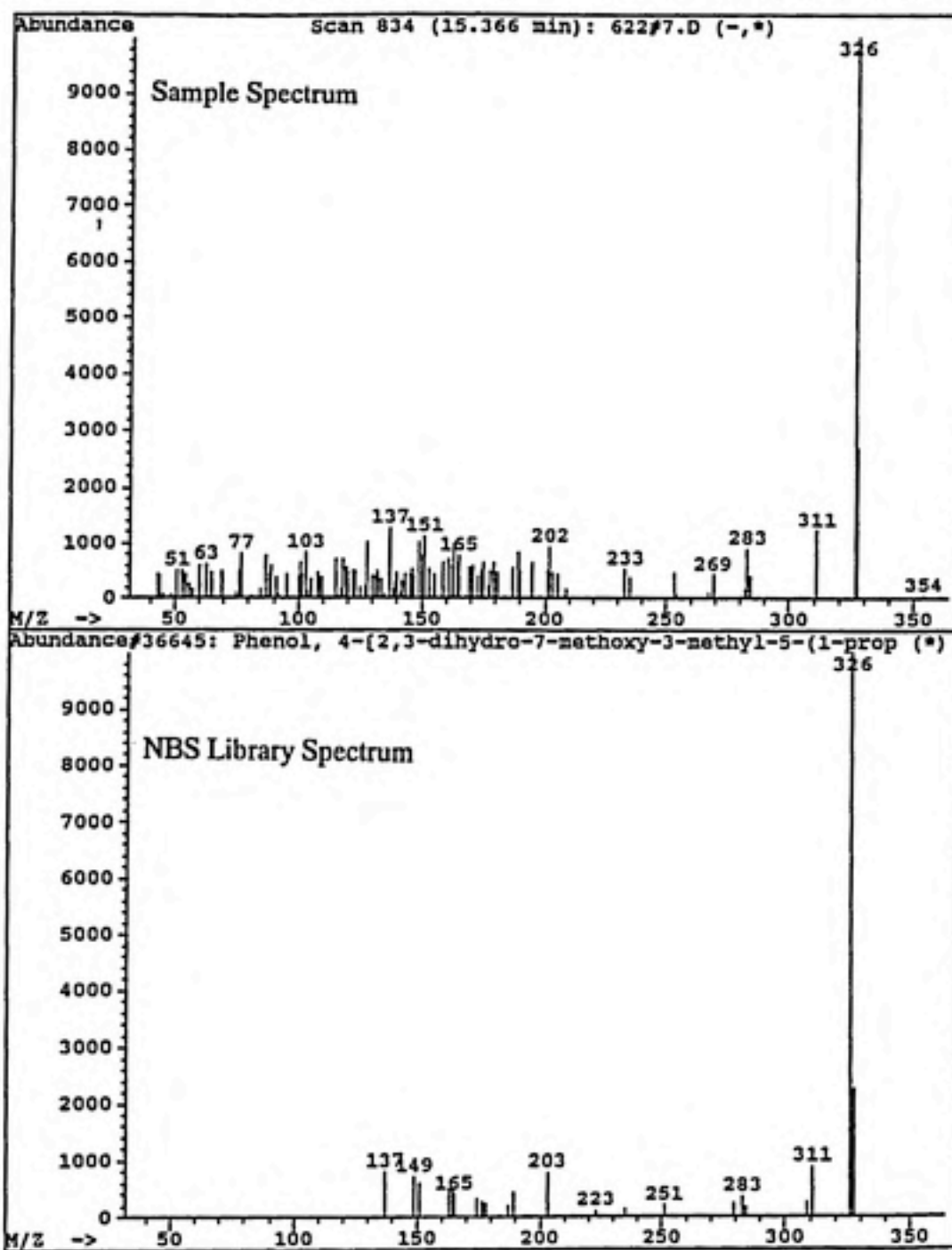


Figure 5.10. Match of unknown M.W. 326 with NBS Library Spectrum

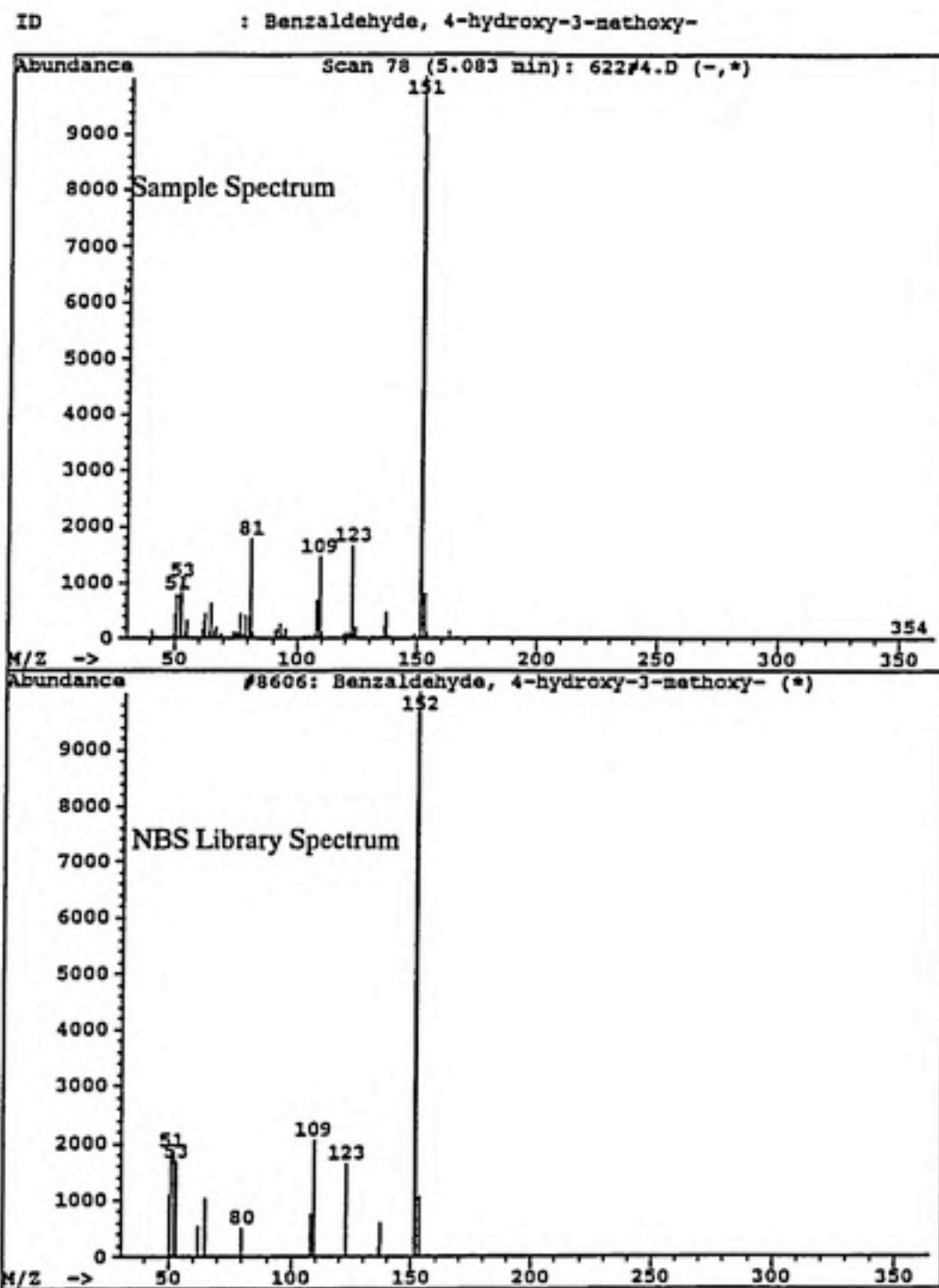


Figure 5.11. Match of unknown M.W. 152 with NBS Library Spectrum

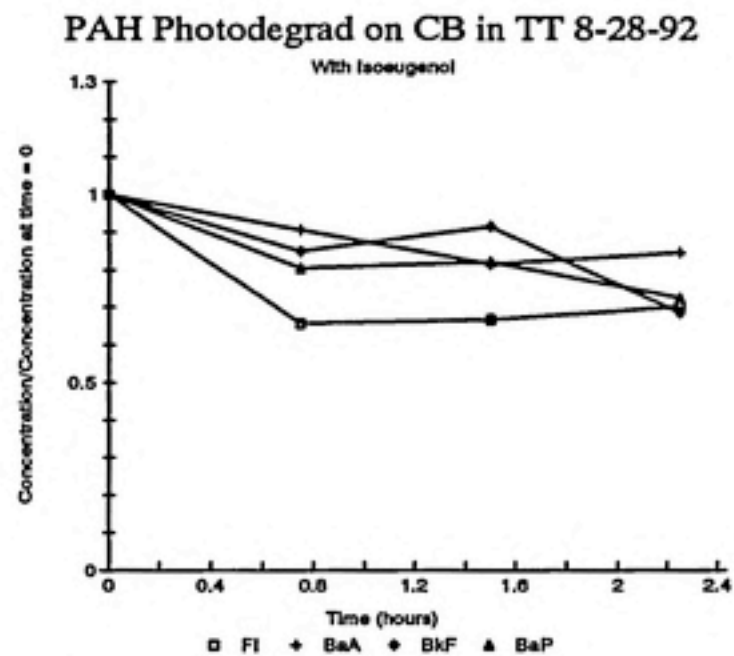
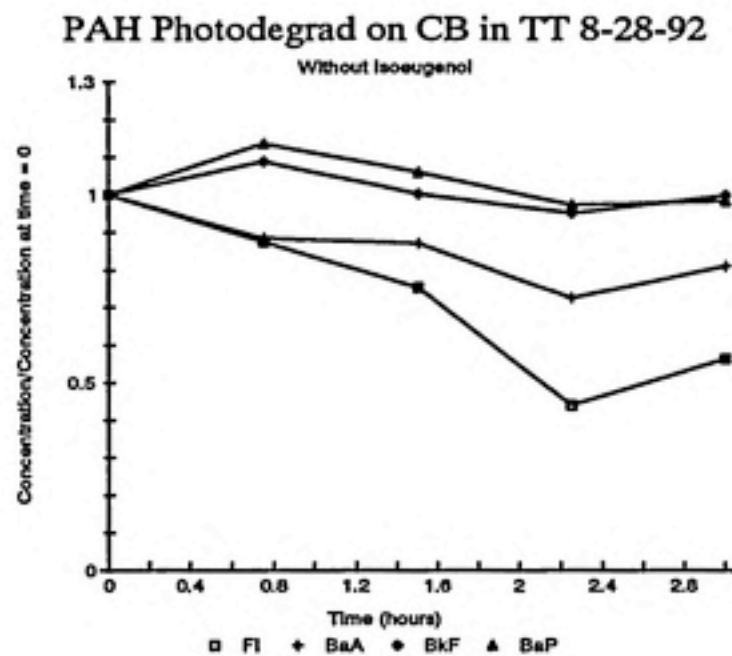


Figure 5.13 PAH Photodegradation without and with isoeugenol

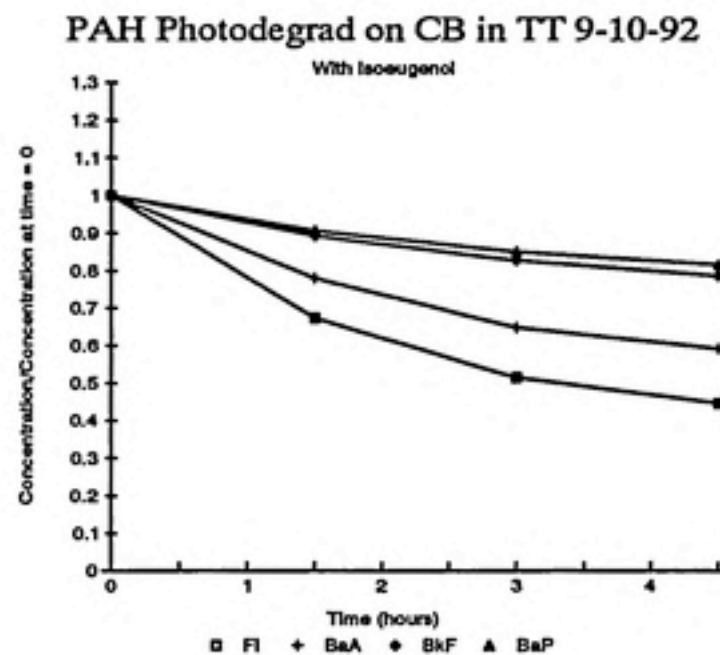
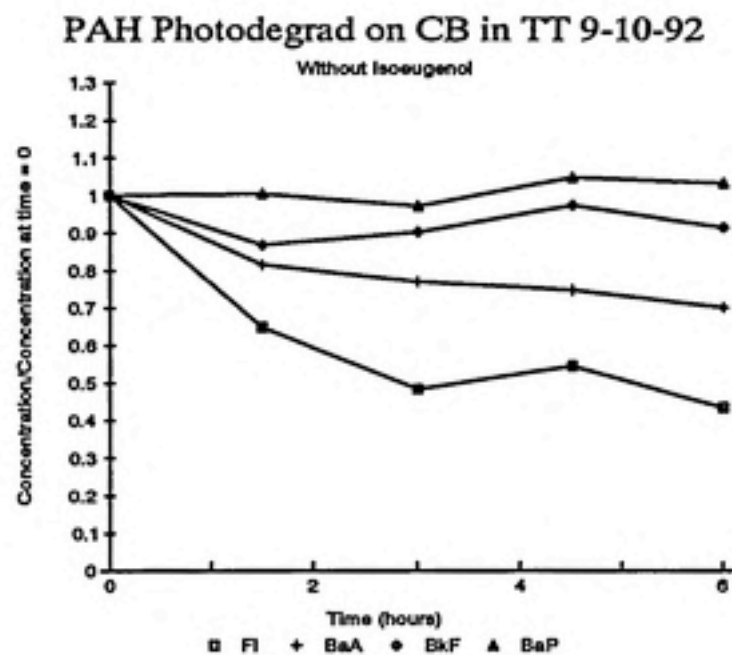


Figure 5.14 PAH photodegradation without and with isoeugenol



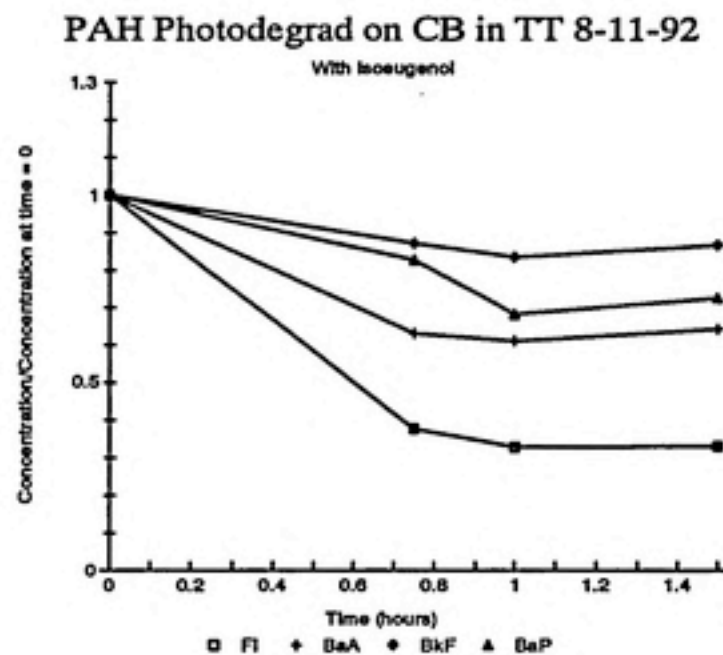
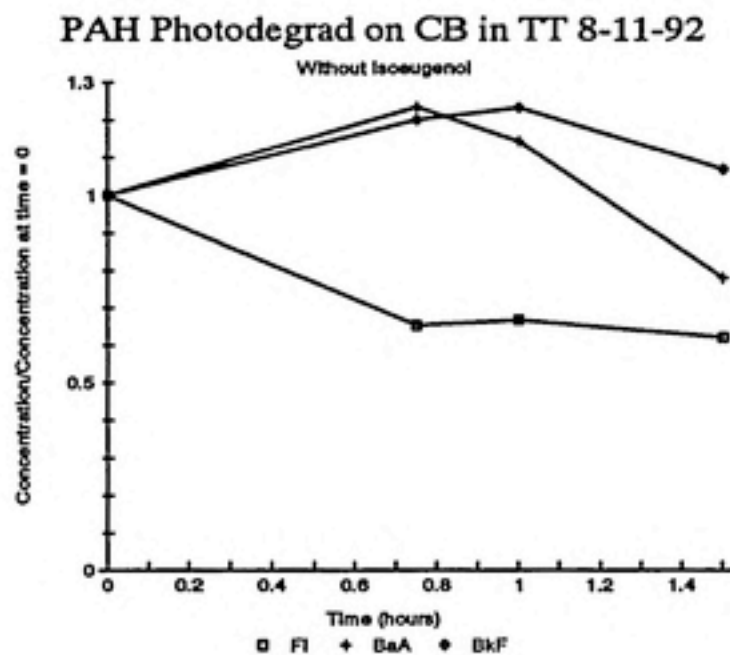


Figure 5.15 PAH photodegradation without and with isoeugenol

Table 5.3. MGLH Regression Results of Model Equation 5.1 for BaP

DEP VAR:	BAP	N:	13	MULTIPLE R:	.684	SQUARED MULTIPLE R:	.468
ADJUSTED SQUARED MULTIPLE R:	.419	STANDARD ERROR OF ESTIMATE:	0.0777689				
VARIABLE	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)	
TIME	0.0031915	0.0067498	0.1157108	0.80822	0.47284	0.64557	
TIME*							
ISO	-0.0457587	0.0154130	-0.7265219	0.80822	-2.96885	0.01277	
ANALYSIS OF VARIANCE							
SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P		
REGRESSION	0.0584290	2	0.0292145	4.8304413	0.0312134		
RESIDUAL	0.0665280	11	0.0060480				

Table 5.4. MGLH Regression Results of Model Equation 5.1 for BaA

DEP VAR:	BAA	N:	13	MULTIPLE R:	.925	SQUARED MULTIPLE R:	.856
ADJUSTED SQUARED MULTIPLE R:	.843	STANDARD ERROR OF ESTIMATE:	0.1181746				
VARIABLE	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)	
TIME	-0.0546983	0.0102567	-0.6787843	0.80822	-5.33294	0.00024	
TIME*							
ISO	-0.0732622	0.0234209	-0.3981441	0.80822	-3.12806	0.00961	
ANALYSIS OF VARIANCE							
SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P		
REGRESSION	0.9129527	2	0.4564763	32.6866036	0.0000235		
RESIDUAL	0.1536177	11	0.0139652				

## BaP Photodegradation w/ no iso

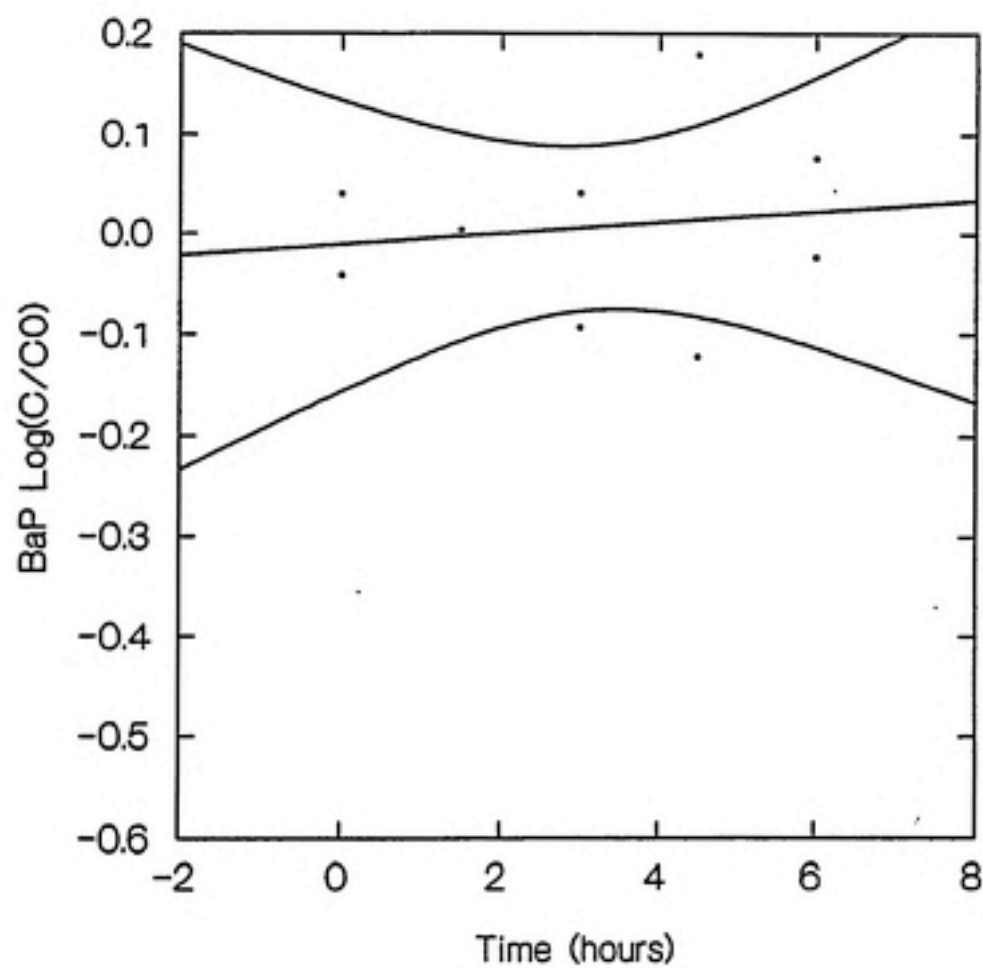


Figure 5.16a. CI, Regression Line and Data for BaP with no Isoeugenol

## BaP Photodegradation w/ iso

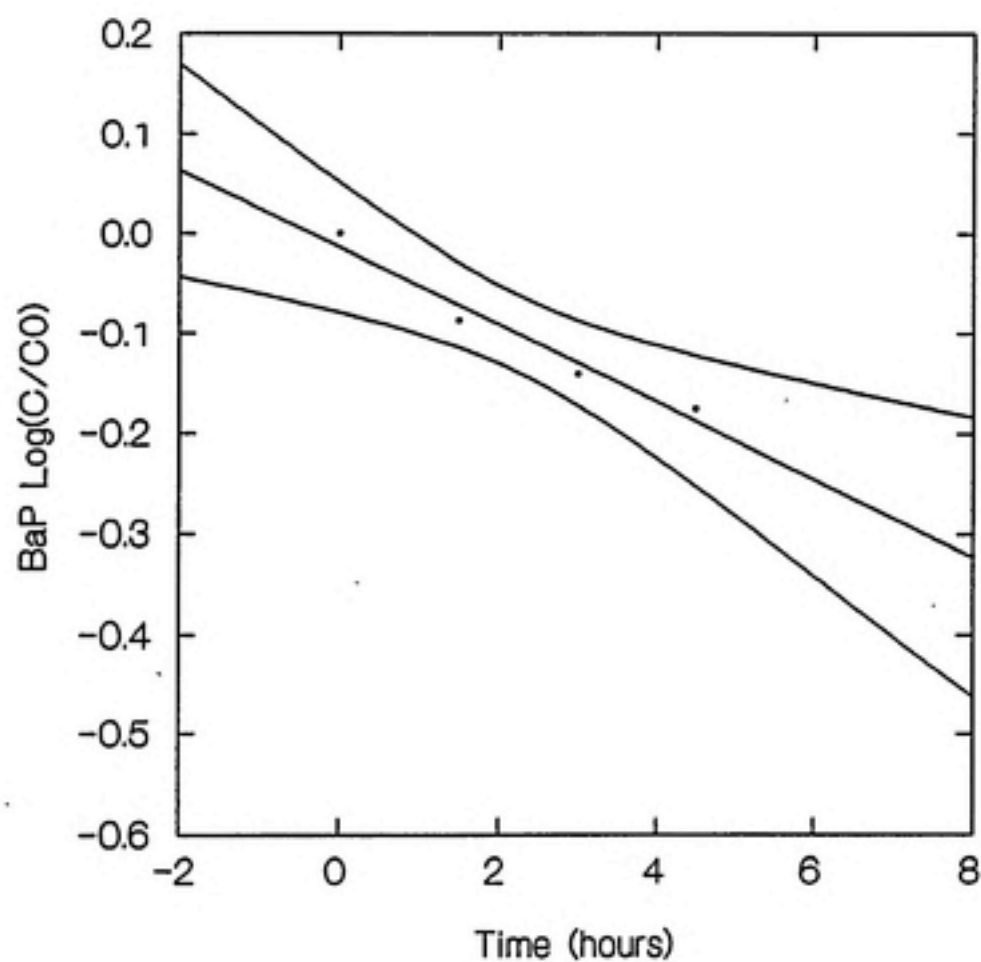


Figure 5.16b. CI, Regression Line and Data for BaP with Isoeugenol

## BaA Photodegradation w/ no iso

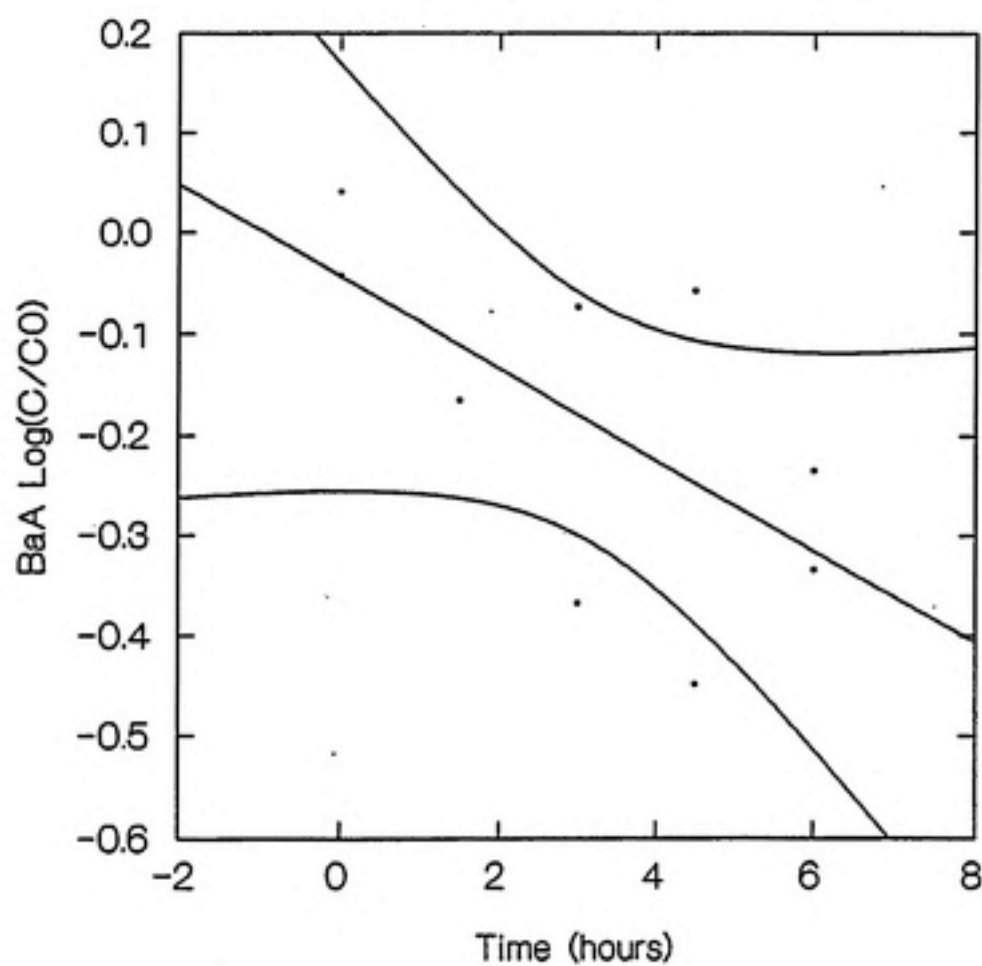


Figure 5.17a. CI, Regression Line and Data for BaA with no Isoeugenol



## BaA Photodegradation w/ iso

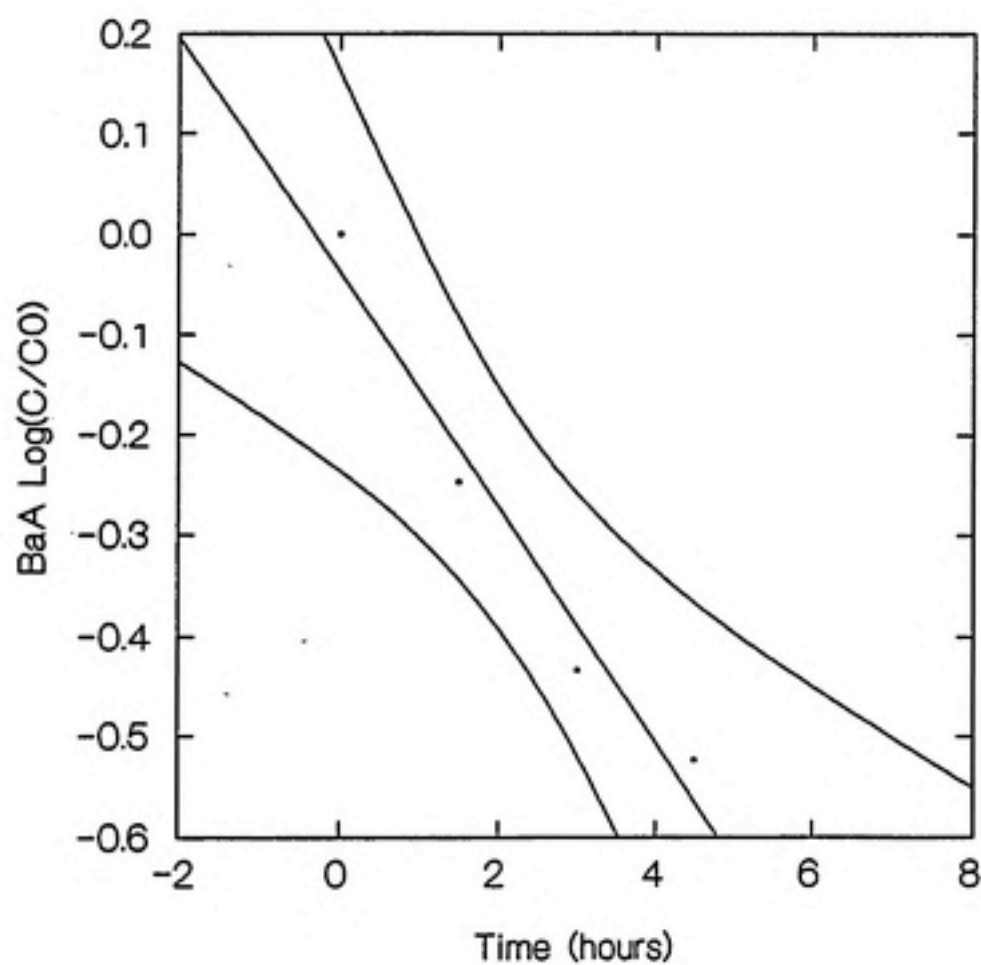


Figure 5.17b. CI, Regression Line and Data for BaA with Isoeugenol

## 6. Summary and Conclusions

A method has been developed to evaluate PAH reactivity on heterogeneous combustion aerosol particles as a function of specific physical and chemical properties which are representative of the character of the PAH environment. PAHs represent from 0.5 to 5 % of the organic fraction of combustion aerosols. Photolysis during transport of PAH on combustion particles can lead to a loss of carcinogenic species (Nielsen et al., 1988) or an increase in the amount of mutagenic species (Finlayson-Pitts & Pitts, 1986). There is current disagreement concerning PAH particle phase reactivity in atmospheric systems (Behymer & Hites, 1988). Combustion particles from different combustion sources vary in chemical and physical properties. Although varying in composition, combustion particles typically consist of an elemental carbon core surrounded by an adsorbed organic layer.

This investigation of particle associated PAH photo-reactivity addresses the role of associated organic compounds in addition to the role of elemental carbon surfaces in determining the reaction rate. A method was developed to incorporate different compounds and the amounts of these constituents in the organic coating on different types of particle surfaces. This was done so that realistic PAH environments on combustion soot particles could be generated and studied.

Model irradiation conditions and model combustion particles were generated to reduce the complexity inherent in combustion particles. The criteria for the model system were that particles were consistently generated, that organic composition could be easily modified, and that particles were readily accessible to exposure to ultraviolet radiation. The method involved use of a liquid phase adsorption technique to prepare

uniform multicomponent organic coatings on carbon black particles, and to uniformly distribute the particles on to Teflon filters. Particles were exposed to light in a turntable photoreactor and subsequently analyzed for evidence of PAH photodegradation over time.

To obtain results which were relevant to real combustion particles, factors influential to the measurement of photodegradation rates of adsorbed polycyclic aromatic hydrocarbons were evaluated. Particle surface characteristics, identity and concentration of organic constituents, and PAH stability in the dark were examined to determine their effect on the measured photodegradation rates. In the dark, PAH coated on carbon black (using a liquid suspension coating technique) did not show any appreciable decay over a period of three hours. The surface characteristics of the substrate were determined to influence the photodegradation rate of adsorbed PAH. PAH were observed to be more photoreactive when adsorbed on filters than when adsorbed on carbon black. On the basis of dark experiments, PAH degradation in the reactor was attributed to photochemical reactions and not to thermal reactions influenced by either the carbon black surface or the filter surface processes. Choice of solvent, transfer method, type of filter, and organic concentrations were made to optimize PAH and other organic constituents adsorption to the carbon black surface. Suspensions of the particles and coating organics in dichloromethane, followed by collection on a Teflon filter in a Buchner funnel, proved to be the best method for coating and collecting particles.

The influence of co-adsorbed organic compounds on the rate of PAH photodegradation on carbon black particles was measured. PAH photodegradation in solution was known to be enhanced by the presence of methoxyphenols. Methoxyphenols are known constituents of the extractable organic layer found on wood combustion particles. In the presence of isoeugenol, BaP on carbon black particles had

a half-life in the photoreactor of 14 hours. Under the same photoreactor conditions BaP on carbon black without isoeugenol was stable and did not react.

This implies that the methoxyphenol mediated PAH photodegradation processes, observed in solution and on these model particles, may also occur in the atmosphere on combustion particles.

The method developed in this study allows evaluation of the importance of the particle surface and composition of the organic layer to the photodegradation processes which may occur on combustion particles in the atmosphere. Based on the chemical and physical character of combustion particles the reactivity of adsorbed PAH may be evaluated to determine the transport, fate, and potential health implications of emitted particulate matter from various combustion sources.

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