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A Study of Polycyclic Aromatic Hydrocarbons During Combustion in an AFBC System

Laura Dicken

Western Kentucky University

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A STUDY OF POLYCYCLIC AROMATIC HYDROCARBONS
DURING COMBUSTION IN AN AFBC SYSTEM

A Thesis Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Laura Ann Dicken
December 1997

A STUDY OF POLYCYCLIC AROMATIC HYDROCARBONS
DURING COMBUSTION IN AN AFBC SYSTEM

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Laura Ann Dicken

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A STUDY OF POLYCYCLIC AROMATIC HYDROCARBONS
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48 Pages

Directed by: Wei-Ping Pan, John T. Riley, and Eric Conte

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The purpose of this study was to develop the on-line method of analysis which leads to the study of polycyclic aromatic hydrocarbons (PAHs) during combustion in an atmospheric fluidized bed combustor (AFBC) system. The study of PAHs is important because they may be produced upon the combustion of coal. The US EPA prioritizes PAHs as major pollutants due to their mutagenic and carcinogenic effects. Standards of PAHs were analyzed by injection into the gas chromatograph-mass spectrometer (GC-MS). These standards were then analyzed using the on-line method. Two coals were burned in the AFBC system and effluent samples were collected. These were analyzed with the GC-MS to see if there were any PAHs or chlorobenzenes present.

I. INTRODUCTION

A. Background

There has been much work done and many studies performed on coal since it became so widely used in power stations and boilers. The polycyclic aromatic hydrocarbons (PAH) which may be produced in coal combustion are important pollutants because of their known carcinogenic and mutagenic effects as prioritized by the US EPA.¹⁵ Over the past two decades most of the papers published focus on the output from coal-fired power stations. There are about forty organic compounds that were found to be common among many of the studies performed. However, there is no standard method of testing available; consequently, the results are often conflicting. Therefore, a standard method of testing is needed.

B. Polycyclic Aromatic Hydrocarbons

There are many organic materials which have chemical structures that are able to form polycyclic aromatic compounds (PAC) under two conditions; these conditions are pyrolysis¹ and combustion.² There are two complementary structures which make up the organic matter of coal. A macromolecular, insoluble, three-dimensional network composed of condensed aromatic and hydroaromatic units connected by short alkyl bridges and ether and thioether linkages. The other component is a molecular phase of compounds of low to medium molecular mass and generally soluble in organic solvents. The molecular component described in the second component of structures that make up the organic matter of coal

consists of varying amounts of aliphatic hydrocarbons, hydroaromatic and polycyclic aromatic hydrocarbons, heterocyclic compounds and polycyclic aromatic compounds.

Chemical changes such as contraction-swelling, devolatilization, decarboxylation, changes in fluidity and plasticity occur when coal undergoes pyrolysis and some of the products are released into the atmosphere. Along with these chemical changes, further aromatic clusters can be formed as a consequence of the thermal process. These inherent aromatic hydrocarbons and those formed during the process are major atmospheric pollutants. Polycyclic aromatic hydrocarbon molecules can exist in the gas phase (<6-ring PAH), in the solid phase (>6-ring PAH) or in both phases (4- and 5-ring PAH) in the air depending on their molecular mass.²

Coal structure undergoes chemical and physical changes when heated and a fraction is released; these fractions undergo cyclization reactions³ leading to polycyclic compounds that can exist in the gas and in the solid phase, depending upon the environmental temperature and their molecular volume.⁴

The following are the two possible sources of PAC formation in coal combustion:

- (1) incomplete combustion, in which fragments of the mostly aromatic structure of the coal are emitted;
- (2) as a consequence of the chemical changes during combustion, reactions such as cyclization of radical condensation⁵ and alkyl chains can lead to polycyclic compounds through polymerization reactions, which are favored over oxidation in fuel-rich regions of the flame.⁶

The mechanisms in the combustion process for producing polycyclic aromatic hydrocarbons (PAH) are complex, but it appears that the chemical reactions in flames proceed by the radicals released during the pyrolysis which precedes combustion. Synthesis mechanisms for PAH from C_2 species to benzo[a]pyrene have been suggested by some studies,^{7,8} but very similar pathways can and may lead to most of the PAHs produced in coal combustion and are referred to as carcinogens and mutagens due to their harmful effects.⁹

The earliest and most simple PAH formed can undergo further pyrolytic reactions to form larger, highly condensed PAH by intermolecular reactions, such as condensation and cyclization,¹⁰ depending on the flue gas conditions. As a result, the PAH formed can exist in the gas emitted or be supported on particulate matter, or could give rise to particulate matter, depending on their association.¹¹

Depending upon the meteorological conditions, these small particles may be able to travel long distances in the atmosphere. Some of the PAHs photodecompose very quickly in the atmosphere due to their high reactivity in ozone, while the more stable PAHs can exist for longer periods of time.¹²

According to a study done by Lloyd and Purushothama,¹³ modern coal-fired boilers do not usually discharge significant amounts of organic coproducts. Volatile organics are always produced and almost always completely burned as a part of the combustion process. Combustion of these volatiles typically takes place within about 100 milliseconds, which is an order of magnitude less than the typical residence time of the ascending vapors in the bed. However, with older boilers, there are conditions which can give rise to the discharge of organic compounds. Phenomena such as bubbling and slugging, or localized reducing areas near the points of fuel injection, can produce oxygen-deficient zones from which unburned or partially burned hydrocarbons may escape. These occurrences typically relate to boiler

design: old chain-grate boilers are notoriously “dirty.” In addition they can be affected by abnormal operating conditions, such as temperature and oxygen supply, especially during start-up and shutdown.

Among the 37 papers examined, the distribution of some 440 organic compounds is highly skewed. Three hundred of these compounds were reported in individual publications and not confirmed by any of the other 36 papers. On the other hand, 13 organic compounds were identified in ten or more studies. Each of the 13 compounds reported in ten or more papers (anthracene, benz[a]anthracene, benzo[ghi]perylene, benzo[a]pyrene, benzo[e]pyrene, chrysene, coronene, fluoranthene, fluorene, naphthalene, perylene, phenanthrene, and pyrene) is a polynuclear aromatic hydrocarbon. These results reflect the organic structure of coal itself, mainly a collection of aromatic and hydroaromatic rings. It also reflects the uncommon thermal stability of PAHs especially those with compact and symmetrical structures.

C. Other Research

The awareness of environmental impacts caused by fossil fuels has been increasing more and more due to the utilization of renewable energy resources. The focus of intensive research in many countries is the power production from biomass with integrated gasification combined cycle (IGCC) and also the utilization of the product gas from biomass gasification as a fuel in diesel power plants.

A major problem in biomass gasification is the formation of tar compounds, such as hydrocarbons heavier than benzene (MW 78). The typical total tar contents of fluidized bed gasification of biomass are in the range of 2-10gm_s⁻³. High-molecular weight polyaromatic compounds with a molar mass of >200 and a boiling point of >350°C are called heavy tar compounds in this study. The content of these compounds in fluidized bed gasification of

pine sawdust has been determined to be in the range of $0.5\text{-}2\text{gm}_v^{-3}$. Heavy tar formation can lead to a number of problems such as condensation on the surfaces of pipes and filters. They can also cause problems in gas-fueled engines related to the cleaning of the gas and operation of the gas nozzles. Most of the sampling methods used in gasification research and development projects originate from the different versions of EPA Method 5; EPA method 5 was designed for sampling particulate emissions from combustion flue gases. There is a need for further development in heavy-tar sampling from pressurized processes and the characterization of this material.

The tar samples for the analysis in this study were taken from a PDU-scale fluidized bed gasifier. A number of different types of wood-derived biomass and straw, peat and wood-coal mixtures were sampled to get the product gases (see Table 1). The proportion of coal was always $<50\%$ when gasifying wood-coal mixtures. The sampling method of heavy tar was based on controlled condensation at $150\text{ }^\circ\text{C}$ and atmospheric pressure. A temperature of $150\text{ }^\circ\text{C}$ was selected as the optimum temperature for collecting the major part of tars with a $\text{MW}>200$, heavy tars, without condensing water vapor and too much of the light tars.

The two types of analysis used in the study include gravimetric and gas chromatograph. The gravimetric method consisted of cleaning a 100 mL glass flask which was weighed accurately three times on an analytical balance. At this time 50 mL of the heavy tar sample was measured and filtered into the flask by a cotton wool filter. The wool filter was then rinsed with dichloromethane and the flask was placed in a fume hood. The dichloromethane was allowed to evaporate at room temperature over a 24 hour period; the flask was then reweighed. After all of the solvent had vaporized, the final result was the mean of the four measurements. A blank test and parallel determinations were carried out for the samples.

Table 1. Typical Analysis of the Feedstocks Used in the Gasification Experiments

	<u>Pine sawdust</u>	<u>Pine bark</u>	<u>Forest residues</u>	<u>Wheat straw</u>	<u>Peat</u>	<u>Polish coal</u>
Moisture content (wt%)	6.1-16.0	5.6-6.7	9.1-12.0	6.1	15-19	4-7
Proximate analysis (wt% db)						
Volatile matter	83.1	71.8	76.7	75.8	68.3	31.8
Fixed carbon	16.8	26.6	21.2	18.1	27.4	59.9
Ash	0.1	1.6	2.1	6.1	4.3	8.3
Ultimate analysis (wt% db)						
C	51.0	53.9	52.3	46.1	54.5	75.5
H	6.0	5.8	6.0	5.6	5.6	4.7
N	0.1	0.4	0.6	0.5	1.8	1.3
S	<0.01	0.03	0.04	0.08	0.2	0.7
O (diff)	42.8	38.3	39.0	41.7	33.6	9.5
Ash	0.8	1.6	2.1	6.1	4.3	8.3
LHV (MJ kg ⁻¹ db)	19.0	20.1	19.7	17.2	21.0	29.2

Another method of analysis used in the study was the gas chromatograph. Two different gas chromatographic methods were developed for heavy tar analysis. One of these methods was high-temperature chromatography with a programmable on-column injector and the other method was general chromatography. The high-temperature method used a 5890 Series II gas chromatograph equipped with electronic pressure control, a flame ionization detector at 400°C and an Al-Clad Columns AC 750 column. The general chromatography method used an HP 5890A gas chromatograph and an HP column with a flame ionization detector at 310°C.

The standards for gas chromatograph calibration were found by identifying the polyatomic compounds from the tar sample with an HP 5890A gas chromatograph connected to an Hp 5970 series mass-selective detector. The model compound was used for identification, and the response factor of the compound was determined for quantitative analysis. Five mL of dodecane solution and 20.0 mL of the heavy tar sample solution were pipetted into a 25.0 mL graduated flask. The internal standard used was dodecane.

Other analytical methods had to be used in this study because the gas chromatographic methods did not provide qualitative knowledge of the heaviest tar compounds. Molecular weight distribution of organic compounds can be estimated using gel permeation chromatography (g.p.c.). Calibration samples are required for quantitative g.p.c. analysis, but no suitable commercial chemicals were found to make calibration possible. However, it has been suggested by Lafleur et al.¹¹ that the mass response factors vary very little for a wide range of polycyclic aromatic compounds (PAC) as long as the entire range of wavelengths over which the PAC absorb (236-500 nm) is monitored.

The g.p.c. system consisted of an HP 1050 series h.p.l.c. pump, a Rheodyne injector and an HP 1040M diode array detector. The columns used in this system were Waters Styragel HR2 and HR0.5 connected in series and kept at room temperature. The eluent was dichloromethane and the flow rate used was 1.00 mL/min. An HP ChemStation 9000 series 310 computer using a wavelength of 235-500 nm was used to collect chromatographic data. A test series was performed which consisted of checking the columns with polystyrene standards and different PAC solutions.

Another method used was analytical pyrolysis along with elemental detection; this method was used to determine the C/H ratio. The platinum foil of a CDS Pyroprobe 1000, which was connected by an HP 5890 Series II gas chromatograph to an HP 5921A atomic

emission detector, was used to carry out pyrolysis. The column used was an HP Retention gap, uncoated and deactivated (5m, i.d. 0.32mm), and the temperature program was 8 min at 50°C, 30 K/min to 250°C and 3 min at 250°C. The heating rate was 5000 Ks⁻¹ and the pyrolysis time was 5 sec at temperatures between 400 and 1000°C. The pyrolysis chamber had an ambient temperature of 110°C. The wavelength detected for hydrogen was 496 nm. The reaction gas was oxygen. Calibration of the C/H ratio was performed using toluene and octadecane. Model compounds used in preliminary test were naphthalene, pyrene, and coronene dissolved in dichloromethane.

Carbonization of the sample led to problems in the measurement of the C/H ratio by analytical pyrolysis. The volatiles had too small a C/H ratio because most of the carbon was bound in the pyrolysis residue. As long as the model compound evaporated easily the correct C/H ratio was obtained. Coronene did not evaporate but pyrolyzed and formed a ratio because it already had too high a boiling point. This pyrolysis residue was not analyzable due to the small amount present.

The results of this study consist of the following. The gravimetric method of analysis was found to be suitable for comparing and evaluating the total tar content of the heavy tar samples. This method was suitable for samples which only contained no water. The analysis by the gas chromatograph method gave results that were both qualitative and quantitative. Each peak present in the chromatogram represents at least one compound and the area of the peak relates to the amount present. The problem with this method was that the heaviest tar compounds did not elute from the column. Coronene was the heaviest tar compound eluted. The use of high-temperature gas chromatography significantly increased the yield of heavy tar compounds. The identification of tar compounds with a molecular weight >302 was not possible because the resolution of the mass-selective detector was too low and the model

compounds were not commercially available. The gravimetric method of analysis gave the better results in this study.¹⁶

Another study of PAH emissions as a function of coal variables was performed. Two Spanish coals, a low-rank coal and a high-rank coal, were used. See Table 2 for coal characteristics. The combustion experiments were performed using temperatures ranging from 650 to 950°C in a laboratory fluidized sand bed combustor with a continuous feed (up to 200gh⁻¹).

Table 2. Proximate and Ultimate Analyses of the Coals

	<u>Low-rank coal</u>	<u>High-rank coal</u>
Ultimate (wt%)		
C (daf)	69.4	87.4
H (daf)	5.80	6.05
N (daf)	1.11	1.90
S (db)	6.12	0.26
Proximate (wt% ar)		
Moisture	7.2	1.1
Ash	22.2	50.5
Volatile matter	39.7	19.6
Fixed carbon	30.6	28.8

The procedure used in sampling the PAHs consisted of passing an aliquot of the outlet gas from the FBR through five traps: first cyclone, second cyclone, nylon filter, Teflon filter and XAD-2 resin. Sonicated extraction with dimethyl formamide (DMF) was completed and then the samples were analyzed by fluorescence spectroscopy in synchronous mode and by capillary gas chromatography with a flame ionization detector.

The PAH analyzed were those the US EPA prioritized and that show fluorescence properties. These include: fluorene, benzo[a]pyrene, chrysene, anthracene, acenaphthene, benz[a]anthracene, dibenz[a,h]anthracene, coronene, perylene and benzo[k]fluoranthene. See Tables 3 and 4 for amounts of PAH emitted by both the high- and low-rank coals.

Table 3. Amount of PAH (ng kg⁻¹) Studied Collected in Each Trap and Emitted from FBC with the Low-rank Coal

<u>Temp (°C)</u>	<u>950</u>	<u>900</u>	<u>850</u>	<u>800</u>	<u>750</u>	<u>700</u>	<u>650</u>
Cyclone 1	153.2	240.6	165.1	180.0	695.9	330.8	154.1
Cyclone 2	246.3	269.6	103.1	153.1	84.0	248.8	115.2
Nylon F	150.4	113.8	158.1	196.4	140.2	308.0	224.2
Teflon F	166.4	408.1	524.9	381.7	264.4	138.5	182.3
XAD-2	149.6	92.2	256.7	379.8	286.2	272.7	125.7

Table 4. Amount of PAH (ng kg⁻¹) Studied Collected in Each Trap and Emitted from FBC with the High-rank Coal

<u>Temp (°C)</u>	<u>950</u>	<u>850</u>	<u>750</u>
Cyclone 1	162.0	315.0	98.8
Cyclone 2	218.0	178.4	180.6
Nylon F	180.9	159.3	175.0
Teflon F	118.2	175.3	141.1
XAD-2	122.6	125.6	109.0

The experiments for this study were carried out with a laboratory-scale fluidized bed combustor of 70 mm i.d. and 200 mm bed height, burning 200 g h⁻¹. The combustion temperature was 850°C, excess oxygen was 20% and limestone was added at a limestone/sulfur ratio of 4. The gas flow was twice the minimum fluidization velocity.

The samples to be analyzed in this study were taken with a McLeod capturer of low volume arranged after two cyclones downstream of the combustor. The inside of the capturer consisted of a nylon filter (20 micrometers), then a Teflon filter (0.5 micron, 0.5 cm diameter) and finally an adsorbent-XAD-2 resin or charcoal-using in both cases 150 mg placed in a glass tube plugged with glass wool. All adsorbents and filters were kept in a refrigerator and protected from sunlight until extraction with DMF in order to eliminate photodegradation reactions. Extraction with DMF was performed by ultrasonication and manual shaking for 30 min, with a final volume of 5 to 10 mL.

Synchronous fluorescence spectroscopy and capillary gas chromatography were used to perform the analyses. The spectrofluorimetric equipment consisted of an 8.3W pulse Xe lamp and quartz cells of 10 mm path length. The slit width of excitation and emission used to produce the spectra was 2.5 nm/min. The samples were diluted 80-fold before the spectrofluorimetric analysis.

The gas chromatographic analyses were performed with a flame ionization detector and a DB-1 capillary column of 60 m length, 0.25 mm i.d. and 0.25 micrometer film thickness. Helium was the carrier gas used along with a head pressure of 135 kPa absolute. The detector and injector temperatures were 300°C and the oven temperature program was 60°C for 2 min, 5 K min⁻¹ to 125°C, isothermal for 40 min, 2 K min⁻¹ to 300°C and isothermal for 28 min. The samples were concentrated from 4 mL to 50 μL after solvent evaporation under vacuum. The injected volume was 2 μL, using split mode with a ratio of 30/1.

It was concluded in this study that the incomplete combustion is not the main factor responsible for PAH emission; the conclusion was derived by taking into consideration the difference in coal structure aromaticity. The high-rank coal shows a higher aromaticity, while the low-rank coal has a greater abundance of alkyl chains and ether bridges. The amount of PAH emitted from the high-rank coal combustion is not much higher than that emitted by the low-rank coal; the similar emissions for high and low-rank coals lead to the conclusion that the PAH emitted from incomplete combustion do not seem to be the main contribution to the total PAH emitted.

Another factor that could possibly be affecting PAH emission is the secondary pyrolytic process. In the stream from the reactor and at the reactor top there will be radicals. The abundance of these radicals will be a function of the flow velocity of the outlet gas, the amount of coal fed and the combustion temperature. Data collected on the total emissions of PAH can be seen in Tables 5 and 6.

Table 5. Amount of each PAH studied (ng kg⁻¹) and Total Amounts Emitted from the Low-rank Coal Combustion in the Fluidized Bed Reactor

<u>Temp (°C)</u>	<u>650</u>	<u>700</u>	<u>750</u>	<u>800</u>	<u>850</u>	<u>900</u>	<u>950</u>
Fluorine	1192	838	1274	1442	716	806	1182
Anthracene	759	609	920	801	822	542	577
Pyrene	45	27	141	162	93	119	87
Benz[a]anthracene	70	260	175	167	174	92	110
Chrysene	362	315	427	226	855	304	92
Benzo[a]pyrene	31	58	41	46	157	138	33
Perylene	5	40	44	97	180	42	7
Dibenz[a,h]anthracene	100	56	76	34	168	33	26
Coronene	755	318	463	3384	1621	307	639
Total	3319	2521	3559	6358	4787	2383	2753

Conclusions from this study include the belief that there are two main factors affecting the PAH emissions from coal FBC: the conditions under which the combustion is carried out and the pyrolytic reactions between the radicals formed and emitted at the top of the combustion reactor. The conditions under which the combustion is carried out were shown to have a lower influence, whereas the pyrolytic process has a much greater relevance.¹⁷

Table 6. Amount of Each PAH Studied (ng kg⁻¹) and Total Amounts Emitted from the High-rank Coal Combustion in the FBR

Temp (°C)	<u>750</u>	<u>850</u>	<u>950</u>
Acenaphthene	421	994	391
Fluorene	722	1273	1045
Anthracene	852	778	657
Pyrene	170	44	16
Benz[a]anthracene	238	196	185
Chrysene	471	186	579
Benzo[a]pyrene	13	64	115
Benzo[k]fluoranthene	162	105	173
Perylene	76	27	7
Dibenz[a,h]anthracene	31	70	125
Coronene	1125	612	1113
Total	4284	4351	4408

This study consisted of three coals from different mining areas in N.E. Spain; these coals are labeled Mequinenza, Samca, and Utrillas. The experimental procedure and guidelines for this study are the same as for the previous study, which was performed by the same research team. During the experiments a laboratory-scale fluidized bed combustor of

70 mm inner diameter and 200 mm bed height, burning 200 gh^{-1} was used. A temperature of 850°C was used during combustion, along with 20% excess oxygen and limestone was added to get a limestone/sulfur ratio of 4. The gas flow was twice the minimum fluidization velocity for the experiment.

Samples for the experiment were taken with a McLeod capturer of low volume arranged after two cyclones downstream of the combustor. The capturer contained a nylon filter ($20 \mu\text{m}$), a Teflon filter (0.5 micrometers, 0.5 cm diameter) and an adsorbent-XAD-2 resin or charcoal; in both cases 150 mg was placed in a glass tube plugged with glass wool. The amount of gas sampled includes volumes of 0.746, 0.556 and 0.724 m^3 for Samca, Mequinenza and Utrillas coals respectively; these results correspond to about 4 hours of steady-state operation. Photodegradation reactions were eliminated by keeping all filters and adsorbents in the refrigerator to protect them from sunlight until extraction with DMF.

The analysis procedure for this experiment includes the following steps. First, ultrasonication and manual shaking were used to perform extraction with DMF. The resulting final volume was 5 or 10 mL. Secondly, the analyses were performed with capillary gas chromatography and synchronous fluorescence spectroscopy. The spectrofluorimetric equipment included an 8.3 W pulse Xe lamp and quartz cells of 10 mm path length. A flame ionization detector and a DB-1 capillary column were used in the gas chromatographic analyses.

The data from this experiment included the detection of some of the PAH being studied for standards in this paper. These PAHs include fluorene, and phenanthrene from the Samca coal combustion² (see Tables 7 and 8). The researchers who conducted this study concluded that there is a lack of reported data about atmospheric emissions of organic compounds from coal combustion in power generation.

Due to the volatility of most of the PAH, it may be suggested that not all of them are captured when only physical traps are used to retain these hazardous pollutants. As a result, the stream leaving the cyclone placed at the exit of the fluidized bed combustor was forced through a series of filters with decreasing pore size and then through different adsorbents.²

The emissions of volatile organic compounds from coal utilization cannot be quantified until sampling and analytical techniques are improved.

Table 7. Coal Characteristics and Feed Rates

	<u>Mequinenza</u>	<u>Samca</u>	<u>Utrillas</u>
Ultimate analysis (wt%)			
C (daf)	68.6	71.4	78.9
H (daf)	7.1	6.2	6.3
S _{total} (db)	10.9	5.8	2.1
Proximate analysis (wt% ar)			
Moisture	15.5	15	15.5
Ash	18.8	19	6.9
Feed rate (gh ⁻¹)			
Coal	153	156	122
Limestone	168	94	27

Table 8. Amounts of PAH Detected in the Emissions from Samca Coal Combustion and Trapped Successively by Nylon Filter (20 microns), Teflon Filter (0.5 microns) and Finally, XAD-2

	<u>Nylon 20</u>		<u>Teflon 0.5</u>		<u>XAD-2</u>	
	(ng kg ⁻¹)	(ng m ⁻³)	(ng kg ⁻¹)	(ng m ⁻³)	(ng kg ⁻¹)	(ng m ⁻³)
Fluorene	28	27	49	47	31	29
BaP	7	6	2	2	51	48
BkF	30	123	66	63	157	149
Anthracene	21	20	57	54	27	25
Acenaphthene	218	207	70	66	67	64
Pyrene	trace	trace	trace	trace	83	80

D. Purpose

There are sixteen PAHs that were studied during this research. Standards of five of these PAHs were analyzed for retention times and detection limits using the GC-MS. As stated earlier, there is a need for a standard method of testing. The on-line method of testing was developed; then these five samples were also analyzed by that method. The results of these two methods of analysis were compared. Other samples, such as organic compounds from coal combustion, were analyzed to see if PAHs were detected according to the retention times of the standard PAHs analyzed.

II. EXPERIMENTAL

A. Materials

The materials used in this study include the PAH compounds which were used to derive retention times and detection limits for some of the PAHs. Other materials include organic samples collected on Tenax while different coal samples were being combusted.

For the collection and analysis of organic compounds Tenax, methylene chloride, methanol and several standards were used. TenaxTM-TA, an absorbent resin for trapping volatiles, is 60/80 mesh from Scientific Instrument Services, Inc. This resin has a high temperature limit of 350°C and has a low affinity for water. Hexane, C₆H₁₄ (FW = 86.18), was purchased from Fisher A.C.S. and was certified grade. Methylene chloride (99.6%) CH₂Cl₂ (FW = 84.93), an A.C.S. reagent, was purchased from Aldrich Chemical Company, Inc. Methanol, CH₃OH (FW = 32.04), was 99.9+% A.C.S. HPLC grade, from Sigma-Aldrich. An ultrasonic bath was used for the extractions; this ultrasonic bath was a Cole-Parmer 8851. The glass collection tubes had a 0.5 cm inner diameter and were an average of 35 cm in length. The peristaltic pump was a Masterflex Cole-Parmer 6-600 PRM with solid state speed control.

The standard phenanthrene (FW = 178.23 and BP = 336°C) was 98% and a solid from Aldrich Chemical Co. Chrysene 98% (FW = 228.29 and BP = 448°C) was also used as a standard. It was purchased from Aldrich Chemical Co. Naphthalene 99+% (FW = 128 and BP = 218°C) and acenaphthylene 75% acenaphthylene and 20% acenaphthene

(FW = 152.20 and BP = 280) were purchased from Aldrich Chemical Co. The final standard used was fluorene 98% (FW = 166.23 and BP = 293 °C) purchased from Aldrich Chemical Co.

B. Instrumentation

The instrumentation for the analysis of organic compounds collected from combustion of coal in the AFBC and for the PAH standards is the Shimadzu QP 5000 GC-MS system. An O-I Analytical 4560 Sample Concentrator was used to collect the organic compounds present in samples when analyzed by the on-line method. A Multiple Unit Electric Furnace from Electrical Heating Apparatus Co. was used to volatilize the PAH samples for use in the on-line analysis. This piece of equipment has a maximum temperature of 1900 °C and a safe working temperature of 1800; it was supplied with 110 volts and 5.2 amperes. The temperature for combustion for the on-line analysis was measured by the Omega 2168A Digital Thermometer and the Powerstat Variable Autotransformer, types 3PN176 and 3PN116B. These were produced by The Superior Electric Co.

The major instrument used is the QP 5000 GC-MS system. This instrument was designed and programmed for analyzing samples such as organic samples. The gas chromatograph has connections for two parallel GC columns and a digital splitter. A computer controls the carrier gas flow rate through each of these columns. The viscosity of a gas increases at higher temperatures; thus it is necessary to program the gas pressure in order to maintain the same flow rate throughout the analysis so that the results are not affected as the temperature is increased. One of the two columns leads to the MS interface and the other column to an electron capture detector (ECD) that will eventually be used to perform on-line analysis of the gaseous emissions from the AFBC. The electron impact (EI)

mode of the mass spectrometer operates in the range of 10-700 amu with a standard 70 eV source and is fitted with a 151 L/sec turbo molecular pump; this pumps high capacity facilitates the use of a 0.32 mm capillary column for analysis. The sensitivity of this system may vary depending on operating conditions. The mass fragmentation spectra of detected compounds can be compared with the NIST/EPA/NIH database. This database is made up of spectra of 62,000 compounds including polynuclear aromatic hydrocarbons, chlorinated hydrocarbons, and phenols.¹⁴

The columns in the gas chromatograph system are 0.32 mm in diameter and 60 m in length. The stationary phase consists of Restek Rtx-1 (bonded dimethylpolysiloxane) and has a phase coating with a thickness of 1 μm . The component capacity of this column is approximately 500 ng with a resolution almost as high (84%) as a 0.25 mm diameter column of the same length. The detection and identification of smaller amounts of minor components is possible due to this high resolution. The parallel ECD channel and the GC-MS channel have been calibrated, separately, for pressure/temperature/flow rate relationships from 60°C to 330°C, flow rates between 1.2 to 2.2 mL/min, and pressures up to 400 kPa.¹⁵

C. Experimental Procedure

There were two procedures of analysis used in this study; they are the on-line method and the injection method. The standard PAH compounds were analyzed using both methods in order to get dependable data for retention times and detection limits. The injection method consists of injecting 2 μL of the sample into the column, and the conditions used were included in the program PAH07.MET. The parameters for PAH07.MET are located on page 15. The peaks were then analyzed to see if there were any PAHs present in that particular sample.

The on-line method of analysis includes placing different amounts (in μL) of the sample to be analyzed into a boat which is placed in a glass quartz tube in the combustor. The sample is purged with helium at a rate of 40 mL/minute. The sample is then heated to 400°C and held at these conditions for five minutes. These steps allow any PAHs present to be transferred from the boat into the sample concentrator trap. Both the sample concentrator and the GC-MS are started simultaneously to begin the analysis. After the analysis time has elapsed the resulting peaks are analyzed to determine whether there are any PAH compounds present.

The coals used in this study include 95010 and 95031. Analytical data for coals are in Tables 9 and 10. The atmospheric fluidized bed combustor (AFBC) (see Figure 1) was used for the burning of the two coals.

Table 9. Proximate and Ultimate Analyses Values for the Coals and Limestone Used in the Study

	<u>95010</u>	<u>95031</u>	<u>KY</u> <u>Limestone</u>
<u>Proximate analysis (%)</u>			
Moisture	2.32	8.32	0.19
Ash	7.22	10.78	57.93
Volatile Matter	39.97	37.21	18.90
Fixed Carbon	79.38	52.02	22.98
<u>Ultimate Analysis (%)</u>			
Ash	7.22	10.78	57.93
Carbon	79.38	72.16	11.18
Hydrogen	5.31	4.82	0.16
Nitrogen	1.63	1.54	0.00
Sulfur	0.67	2.38	0.00
Oxygen	5.70	7.57	30.73
Chlorine (ppm)	1039	3070	36.00
BTU/pound	14077	12842	n/a

*Moisture is as-received, all other values are reported on a dry basis.

FLUIDIZED BED COMBUSTOR CENTER FOR COAL SCIENCE - WKU

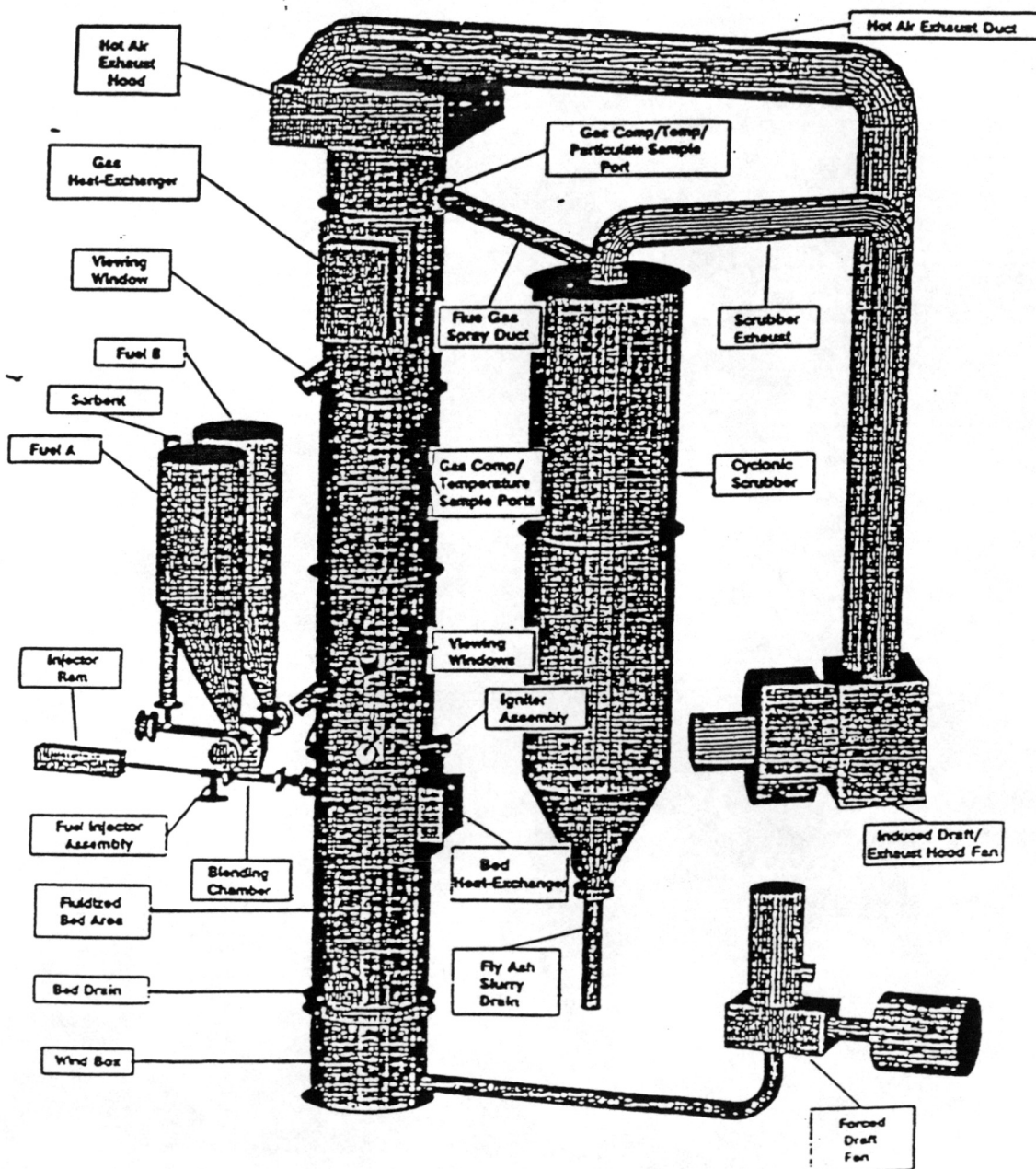


Figure 1. Western Kentucky University AFBC System.

The atmospheric fluidized bed combustor (AFBC) was used for the burning of the two coals above, and organic samples were collected for analysis. For collection of the organic compounds, a glass collection tube was filled with a Tenax resin and plugged on either end with glass wool. The bottom of the glass tube was connected to outlet port 4 from the combustor which is about 54 inches above the setter plate.

Table 10. Analysis of Ashes Prepared from the Coals and Limestone Used in the Study

<u>Metal Oxides</u>	<u>95011</u>	<u>95031</u>	<u>KY Limestone</u>
SiO ₂	49.22	47.32	2.93
P ₂ O ₅	3.36	4.46	2.79
CaO	1.86	1.62	75.60
K ₂ O	4.14	5.03	0.37
TiO ₂	1.11	1.14	0.20
Fe ₂ O	19.90	17.04	0.27
Na ₂ O	0.58	1.90	0.18
MgO	0.70	0.80	3.73
Al ₂ O ₃	17.12	18.18	11.41
MnO ₂	0.02	0.02	0.00

The setter plate is located at the band directly below the bed drain just above the wind box (see Figure 2). The top of the tube was connected to a peristaltic pump. The pump was set at a maximum rate of approximately 0.145 L/min. The pump was calibrated with a wet test meter. In early collections, the steel port outlet of the combustor was connected to the collection tube with Teflon tubing. This sampling system is shown in Figure 2. Later

collections involved connection of the collection tube with a heated steel outlet port and brass compression fittings with a rubber gasket; the collection tube was surrounded by ice. The modern sampling system is illustrated in Figure 3.

After collection of organic compounds on the Tenax resin, extraction was performed by the following procedure using an ultrasonic bath:

- 20 mL of hexane was added to each sample.
- The samples were placed in an ultrasonic bath that contained ice and allowed to sonicate for 2 hours.
- Then an additional 20 mL of hexane was added, fresh ice was also added to the ultrasonic bath and the samples were sonicated for 2 more hours.
- Next, the solution was filtered from the Tenax. The Tenax was washed with the sample solution 2 times and then with fresh hexane 2 times.
- The samples were concentrated for analysis by boiling with boiling chips to 0.5 to 1 mL.

The Tenax samples were analyzed by the GC-MS using the file called TENAX.MET.

The GC/MS method parameters for TENAX.MET are as follows:

Injector temperature: 250.00 °C

Initial oven temperature: 100.00 °C

Oven temperature program:	<u>Rate (°C/min)</u>	<u>Temp(°C)</u>	<u>Time(min)</u>
	5.00	150.00	5.00
	5.00	200.00	5.00
	5.00	250.00	12.35

Initial carrier gas pressure: 106.50 kPa

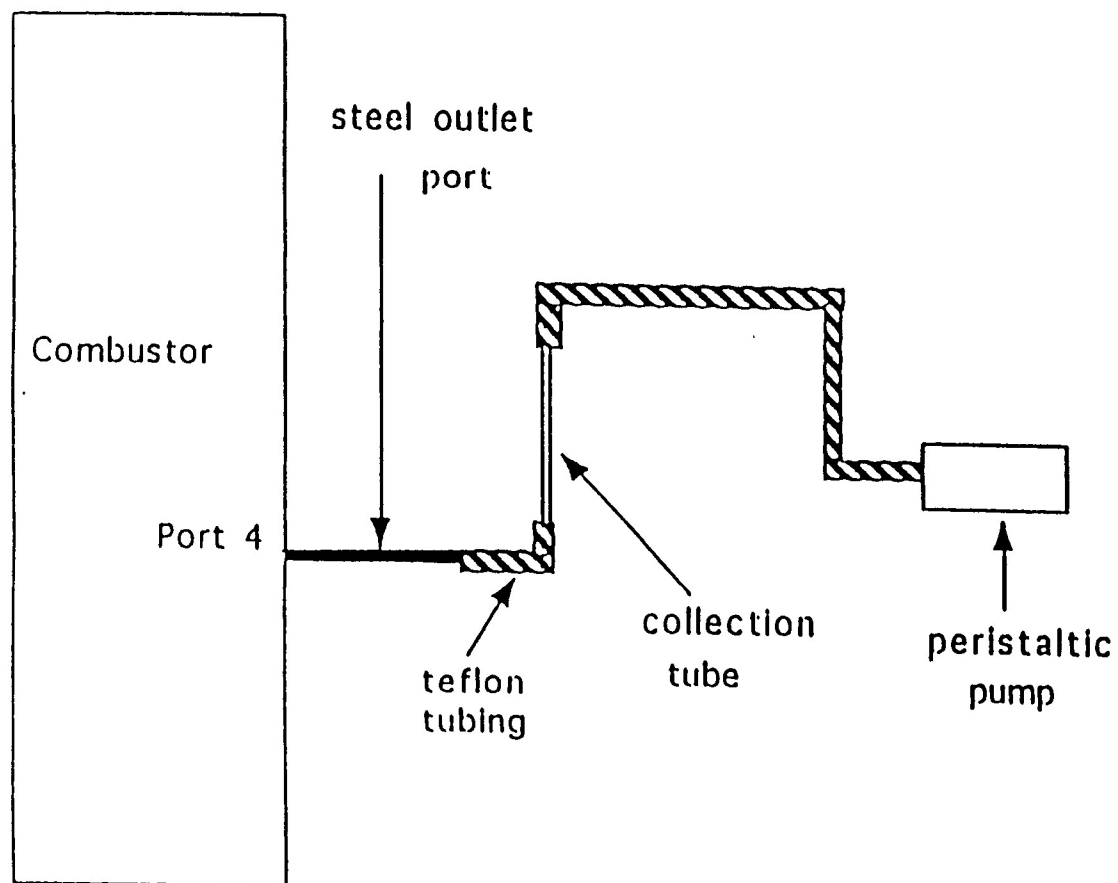


Figure 2. Early organic compound sampling system.

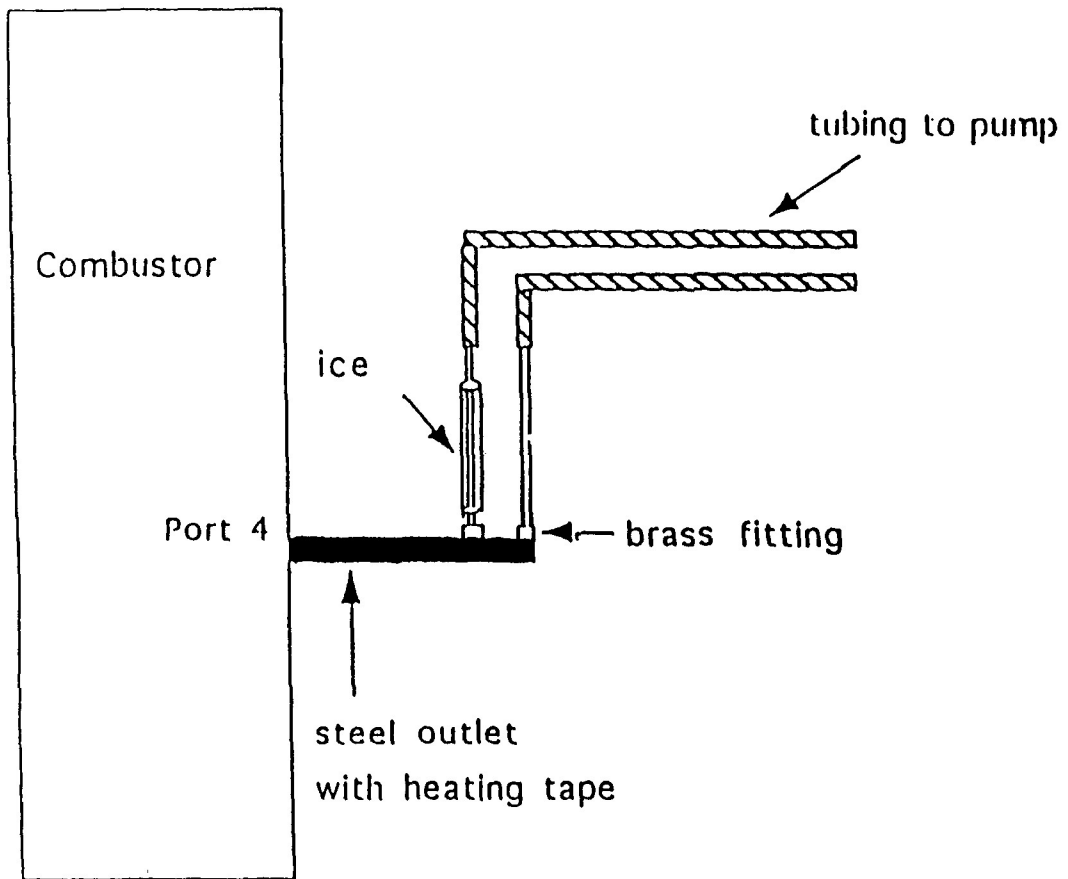


Figure 3. Modified organic compound sampling system.

Pressure program:	<u>Rate(kPa/min)</u>	<u>Press(kPa)</u>	<u>Time(min)</u>
	1.6	122.30	5.0
	1.4	135.90	5.0
	1.2	147.50	12.0

Split Ratio: 10.00

The PAH standard samples were analyzed by the GC/MS using the file called PAH07.MET. The GC/MS method parameters for PAH07.MET are as follows:

Injector temperature: 230.00 °C

Initial oven temperature: 70.0 °C

Oven temperature program:	<u>Rate(°C/min)</u>	<u>Temp(°C)</u>	<u>Time(min)</u>
	8.00	150.00	5.00
	5.00	250.00	5.00
	5.00	280.00	9.00

Initial carrier gas pressure: 95.30 kPa

Pressure program:	<u>Rate(kPa/min)</u>	<u>Press(kPa)</u>	<u>Time(min)</u>
	2.60	121.30	0.0
	1.30	147.30	5.0
	1.00	153.30	9.0

Split Ratio: 10.00

III. RESULTS AND DISCUSSION

Table 11 summarizes some of the parameters of the AFBC burn during which organic compounds and PAHs were studied.

Table 11. Combustion Parameters

<u>Date/Time</u>	<u>Coal/Mixtures</u>	<u>Bed Temp (°F)</u>
8/18/97 3:09-4:09	95010 and Limestone	1550
8/18/97 19:15-20:15	95010 and Limestone and 1% PVC	1550
1/19/97 2:35-3:35	95010 and Limestone and 3.3% PVC	1550
8/19/97 12:48-1:48	95010 and 3.3% PVC	1550
8/20/97 3:20-4:20	95031 and Limestone	1550
8/20/97 10:10-11:10	95031 and Limestone and 1% PVC	1550
8/20/97 16:12-17:12	95031 and Limestone and 3.3% PVC	1550
8/20/97 21:04-22:04	95031 and 3.3% PVC	1550

These samples were analyzed using the program Tenax.Met on the GC-MS for organic compounds, in particular, chlorobenzene and PAHs. There were no PAHs or chlorobenzene

detected during analysis of these samples which were collected on Tenax columns and extracted using an ultrasonic bath. The samples were analyzed using the program TENAX.MET (see page 23).

Table 12 and Figure 4 show the results of the GC-MS analysis of the standard PAH mixture. This standard was analyzed using the method PAH07.MET. These parameters were noted in the experimental section. There were twelve of the 16 PAHs present in the mixture identified when analyzed using the GC-MS. The retention times for these compounds were noted for comparison with the individual standard PAH retention times.

The procedure for making a positive identification using the GC-MS involves (1) printing out the mass spectrum of the peak of interest (the program makes a digital printout that allows for ranking of the main signals quantitatively); (2) comparing the retention time of sample with the retention time of the standard (run with the same method; these usually agree to within ± 0.1 minutes); and (3) looking at the mass spectrum of any standard(s) that match and comparing this with the mass spectrum of the unknown. If the mass spectra are very similar, there is a positive identification. The NIST library gives a similarity index (SI) indicating the degree of similarity between the unknowns spectrum and the spectrum of the real compound from the library. This library was used for the PAH mixture standard.

Table 12. PAH Standard Mixture Results

<u>Peak #</u>	<u>Retention Time (min)</u>	<u>Area x 10⁶</u>	<u>NIST Picks [SI]</u>
4	14.8	2.50	Naphthalene [90]
2	18.8	3.37	Acenaphthylene [91]
1	19.5	2.15	Acenaphthene [91]
1	20.6	2.27	Fluorene [88]
1	23.1	4.02	Phenanthrene [93]
2	23.3	4.22	Anthracene [92]
1	26.2	4.64	Fluoranthene [93]
1	26.8	4.96	Pyrene [92]
1	30.1	4.56	Benz[a]anthracene [90]
4	30.2	4.04	Chrysene [87]
3	33.9	3.57	Benzo[k]fluoranthene [86]
3	33.9	3.11	Benzo[a]pyrene [93]
1	41.1	1.11	Benzo ghi perylene [83]
5	43.0	1.93	Indeno 1,2,3-cd pyrene [91]

Table 13 and Figure 5 contain the data collected using the injection and scan methods of analysis for the standard phenanthrene. The scan method scans the mass spectrum from 10-700 amu. The scan method gave a correlation of 99.8%.

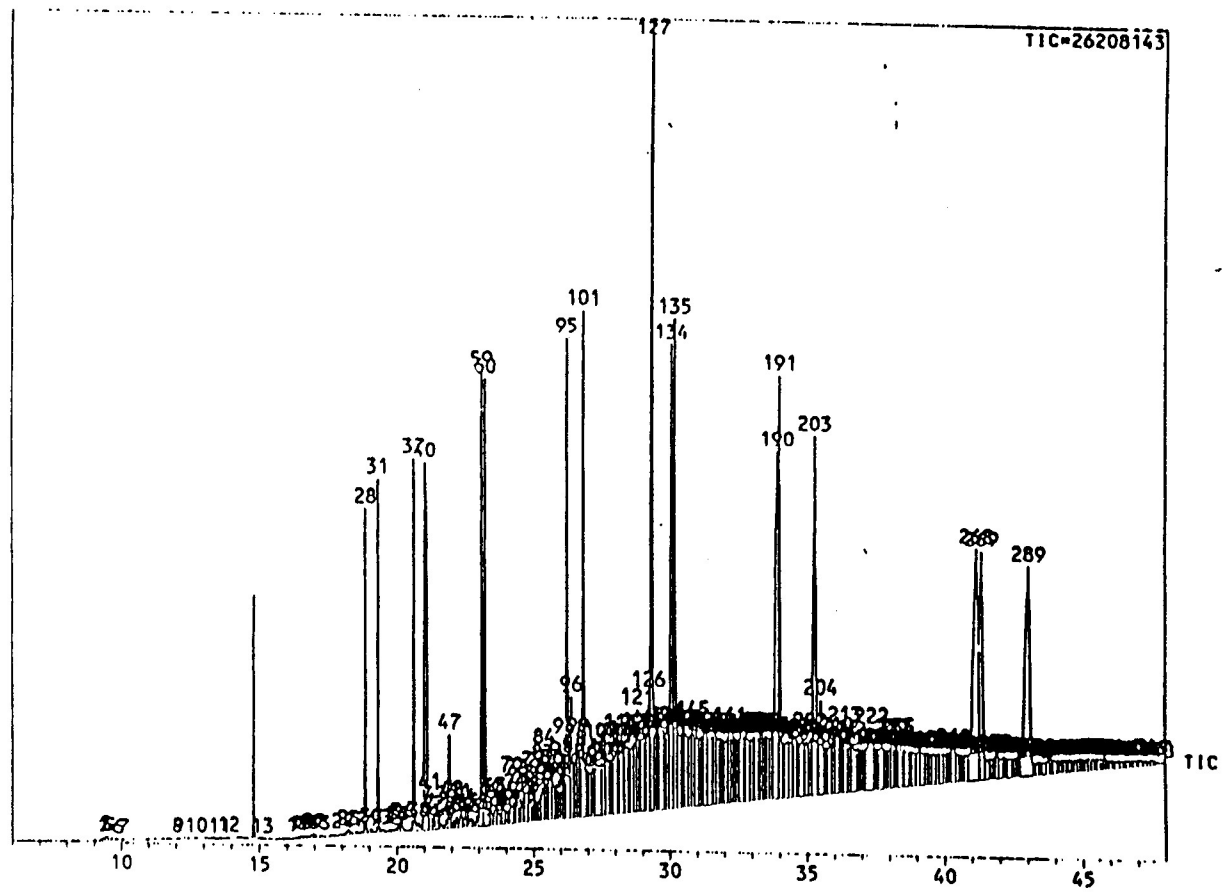


Figure 4. Chromatogram of PAH Mixture

Table 13. Phenanthrene Standard By Injection (Scan)

Conc. (ppm)	Peak #	Retention Time (min)	Area $\times 10^6$	Height $\times 10^6$	A/H (min)
30	1	29.2	1.47	0.19	7.61
40	1	29.2	3.04	0.38	7.96
60	1	29.1	5.63	1.17	5.37
500	3	29.1	46.99	11.17	4.21

Table 14 and Figure 6 are the results from the injection of the standard fluorene. This data was collected using the scan method of analysis. The correlation for this data was calculated to be 94.0%.

Table 14. Fluorene Standard By Injection (Scan)

Conc. (ppm)	Peak #	Retention Time (min)	Area $\times 10^6$	Height $\times 10^6$	A/H(min)
20	1	24.8	1.03	0.14	7.57
30	1	24.7	1.22	0.17	7.31
40	1	24.7	2.27	0.31	7.31
60	1	24.6	4.98	0.70	7.14
500	1	24.7	47.15	12.18	3.87

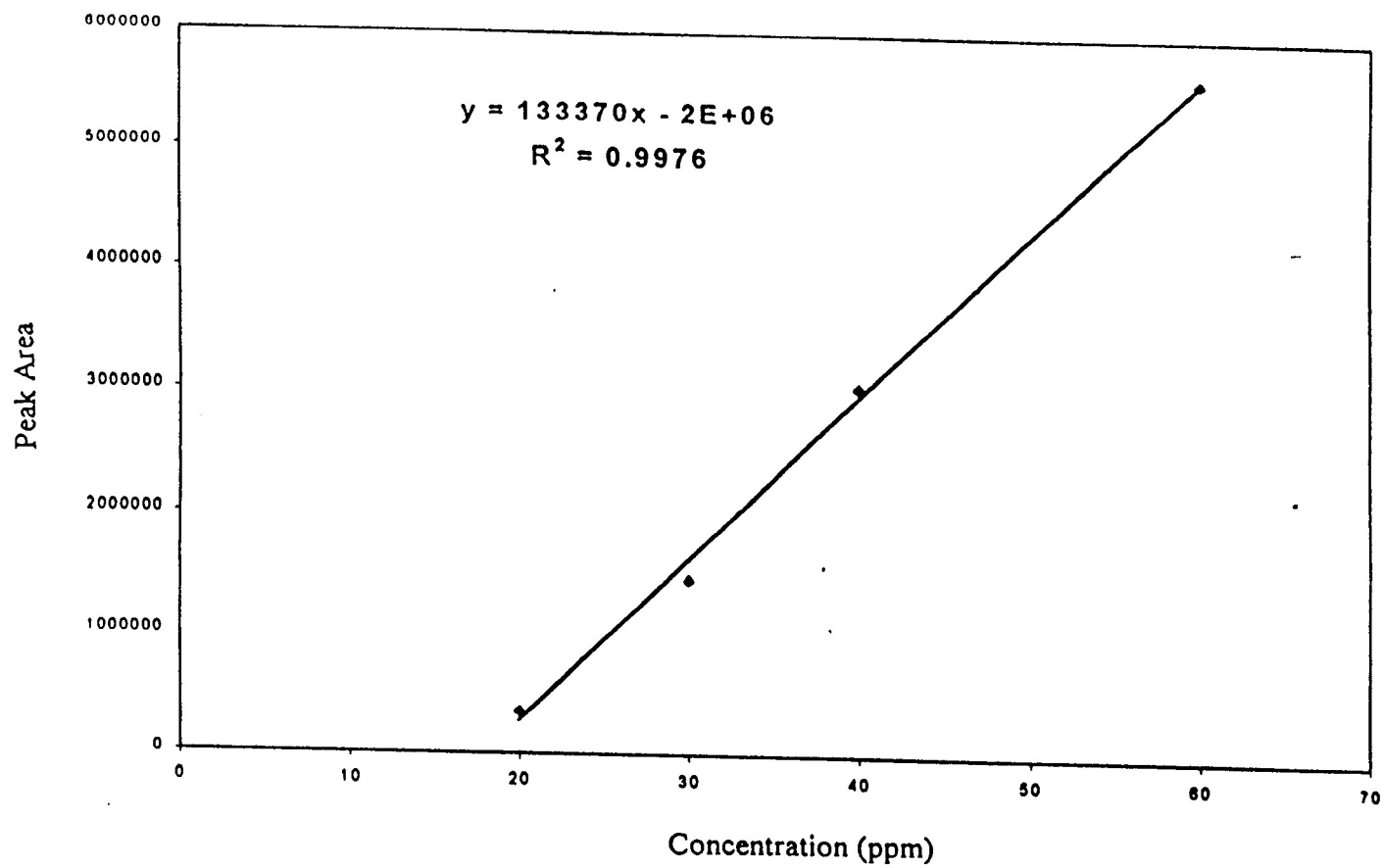


Figure 5 Calibration Curve for Phenanthrene by Injection (Scan)

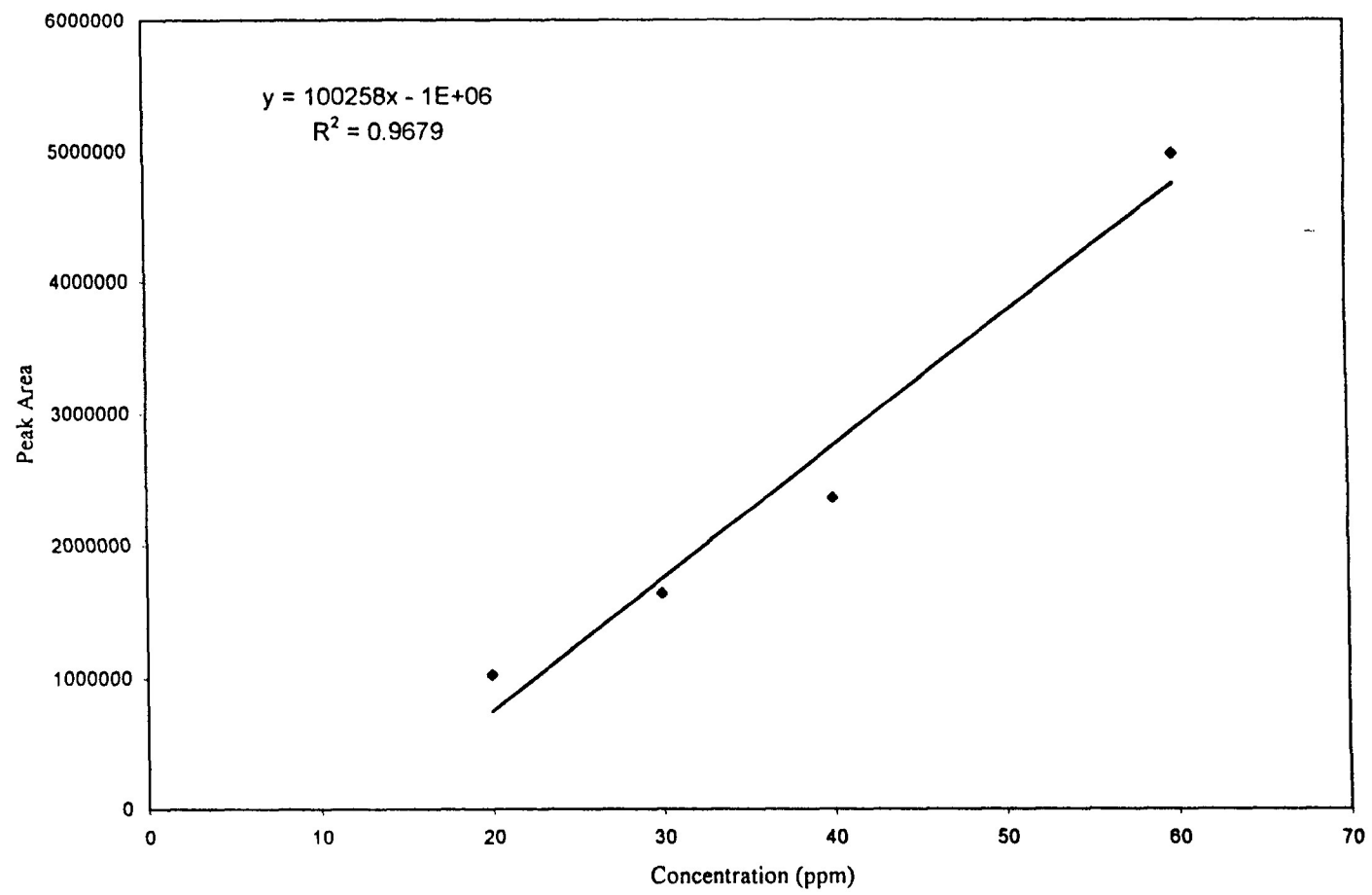


Figure 6. Calibration Curve for Fluorene by Injection (Scan)

Table 15 and Figure 7 contain the data collected using the scan method of analysis after the injection of the standard chrysene into the GC-MS. The calibration curve for chrysene using the scan method had a correlation of 91.1%.

Table 15. Chrysene Standard By Injection (Scan)

Conc. (ppm)	Peak #	Retention Time (min)	Area $\times 10^6$	Height $\times 10^6$	A/H(min)
20	21	46.8	0.30	0.04	6.87
30	8	46.9	0.60	0.10	6.22
40	8	46.7	0.70	0.10	6.88
60	23	46.7	1.73	0.17	10.29
500	6	46.6	44.05	5.48	8.03

Four of the standards were also analyzed by the select ion mode (SIM) of analysis after injection. The SIM mode has some advantages over the scan mode. These include a lower detection limits, a 100 times better signal to noise ratio, and less time to analyze a sample because a certain amu number is entered for the molecular ion peak being searched for. For example, the base peak or molecular ion peak number for phenanthrene is 178, chrysene is 228, fluorene is 165, naphthalene is 128, and acenaphthylene is 152-154. This method gives a better correlation coefficient; when this number is squared the percent correlation is usually 99%. The data collected for the phenanthrene, fluorene, naphthalene, and acenaphthylene injections are given in Tables 16, 17, 18, and 19 and Figures 8, 9, 10 and 11, respectively. The percent correlation for the standards using this method were: phenanthrene - 99.4%, fluorene - 99.9%, naphthalene - 99.8%, and acenaphthylene - 99.9%.

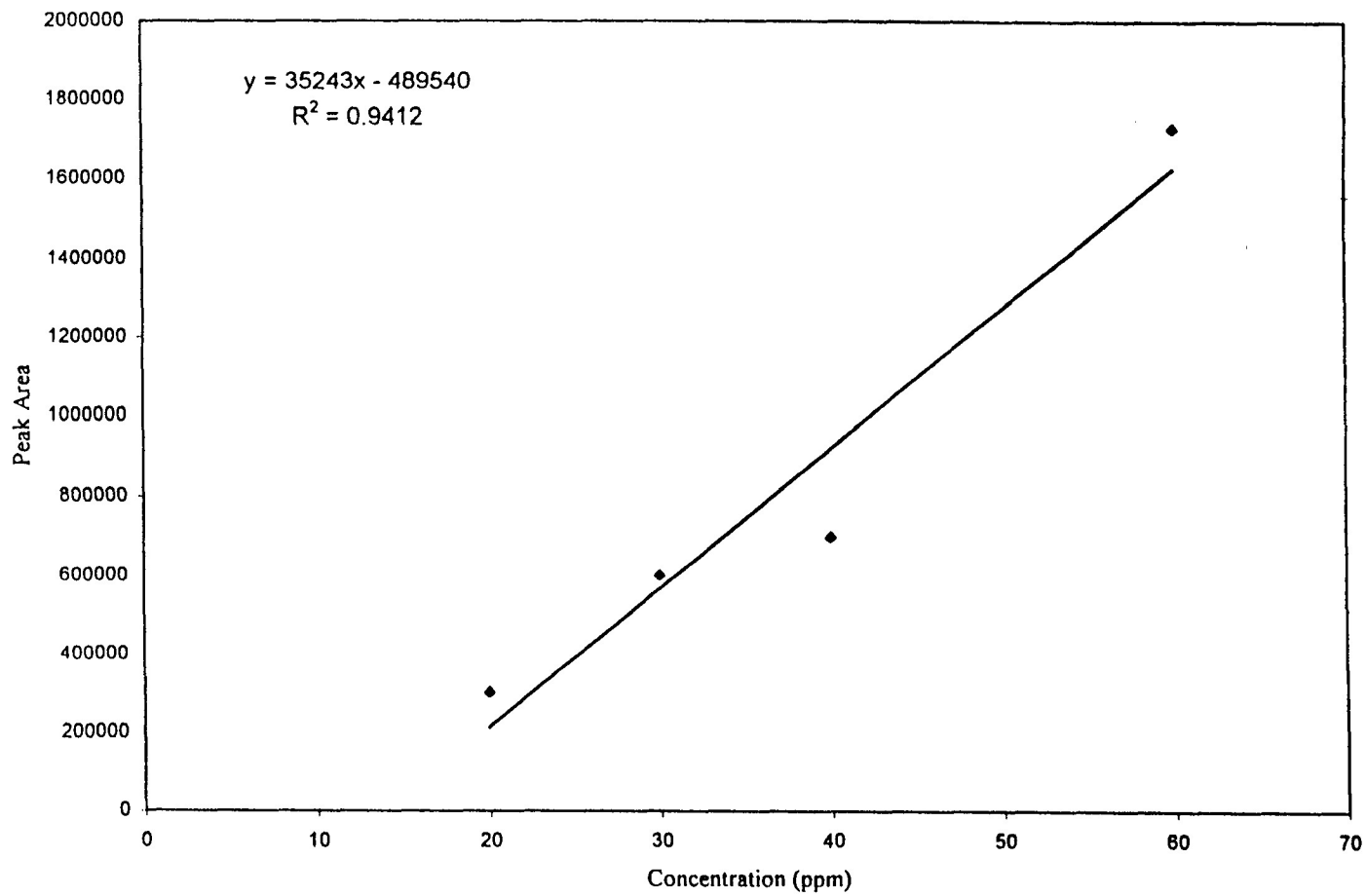


Figure 7. Calibration Curve for Chrysene by Injection (Scan)

Table 16. Phenanthrene Standard By Injection (SIM)

<u>Conc.</u> <u>(ppm)</u>	<u>Peak #</u>	<u>Retention</u> <u>Time (min)</u>	<u>Area</u> <u>x 10⁶</u>	<u>Height</u> <u>x 10⁶</u>	<u>A/H(min)</u>
20	1	29.3	0.41	0.01	10.04
40	1	29.2	0.71	0.07	9.99
60	1	29.1	1.45	0.17	8.62

Table 17. Fluorene Standard By Injection (SIM)

<u>Conc.</u> <u>(ppm)</u>	<u>Peak #</u>	<u>Retention</u> <u>Time (min)</u>	<u>Area</u> <u>x 10⁶</u>	<u>Height</u> <u>x 10⁶</u>	<u>A/H(min)</u>
20	1	24.8	0.48	0.04	10.95
30	1	24.7	0.83	0.08	10.23
40	1	24.7	1.15	0.12	9.33

Table 18. Naphthalene Standard By Injection (SIM)

<u>Conc.</u> <u>(ppm)</u>	<u>Peak #</u>	<u>Retention</u> <u>Time (min)</u>	<u>Area</u> <u>x 10⁶</u>	<u>Height</u> <u>x 10⁶</u>	<u>A/H(min)</u>
20	1	15.0	1.07	0.21	5.00
40	1	15.0	2.05	0.49	4.21
60	1	15.0	2.96	0.77	3.86

Table 19. Acenaphthylene Standard By Injection (SIM)

Conc. (ppm)	Peak #	Retention Time (min)	Area $\times 10^6$	Height $\times 10^6$	A/H(min)
20	1	21.4	0.98	0.21	4.60
40	1	21.5	2.11	0.53	3.98
60	1	21.4	3.09	0.79	3.90

Data collected for the standards were less when analyzed by the on-line method. Ideas were drawn as to why the data was not collectable in some cases. The reason hypothesized is that the sample may decompose or condense on the heated transfer line. Used at this point is a Teflon heat transfer line having a maximum heated temperature of 250°C. The boiling points of the standards tested are: phenanthrene - 340°C, chrysene - 448°C, and fluorene - 295°C, naphthalene - 218°C, and acenaphthylene - 280°C. Since most of the boiling points of the standards are higher than 250°C, a different type of heated transfer line must be used. The two possibilities being considered are copper and steel. Steel will likely be tried first; if there is no secondary reaction between the compound and the steel this type of heat transfer line should be very successful for getting the compound from the furnace to the purger.

The data collected using the on-line method of analysis are given in Tables 20, 21, 22, 23 and 24. Included are the standards fluorene, phenanthrene, chrysene, naphthalene, and acenaphthylene.

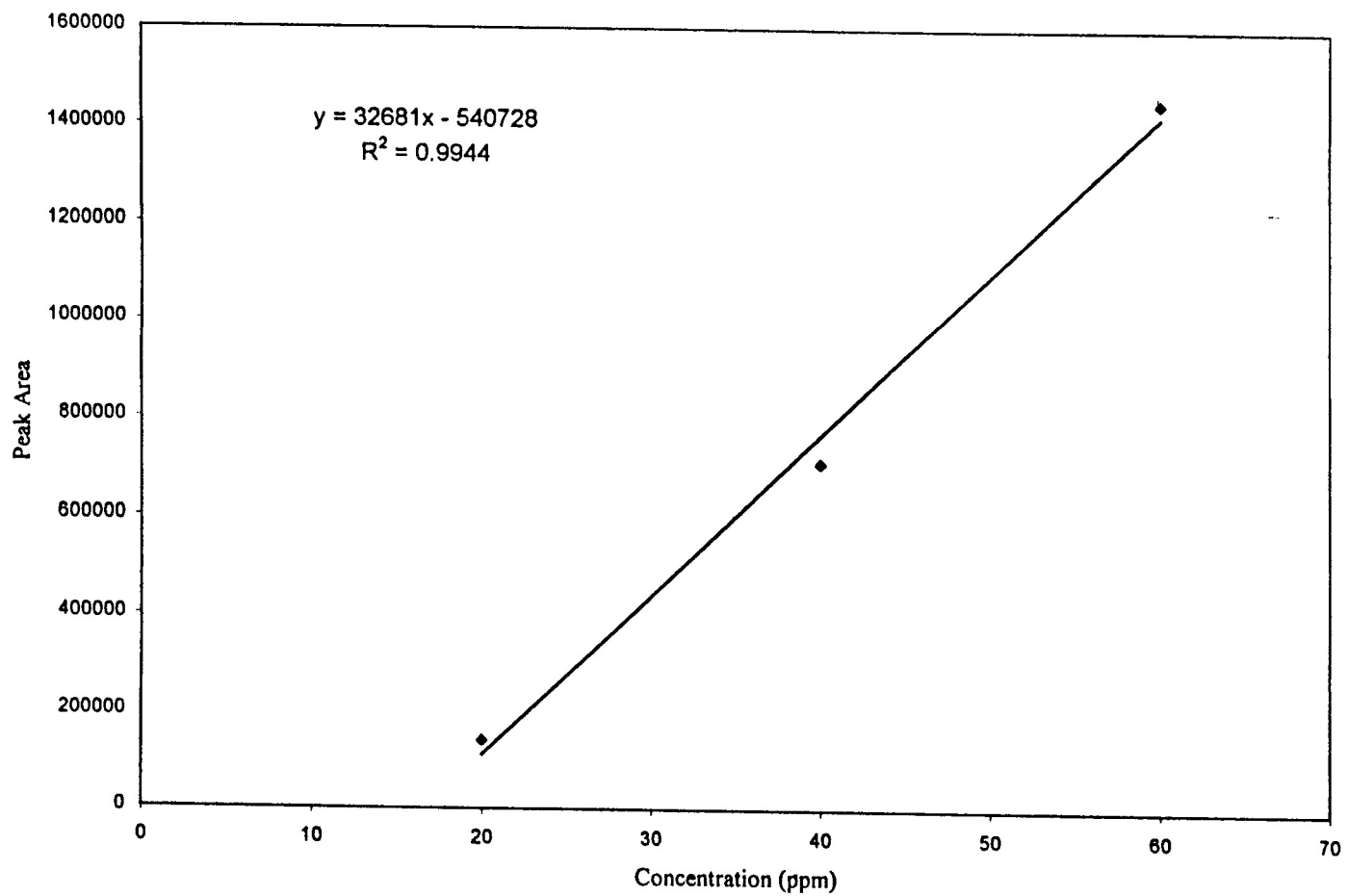


Figure 8. Calibration Curve for Phenanthrene by Injection (SIM)

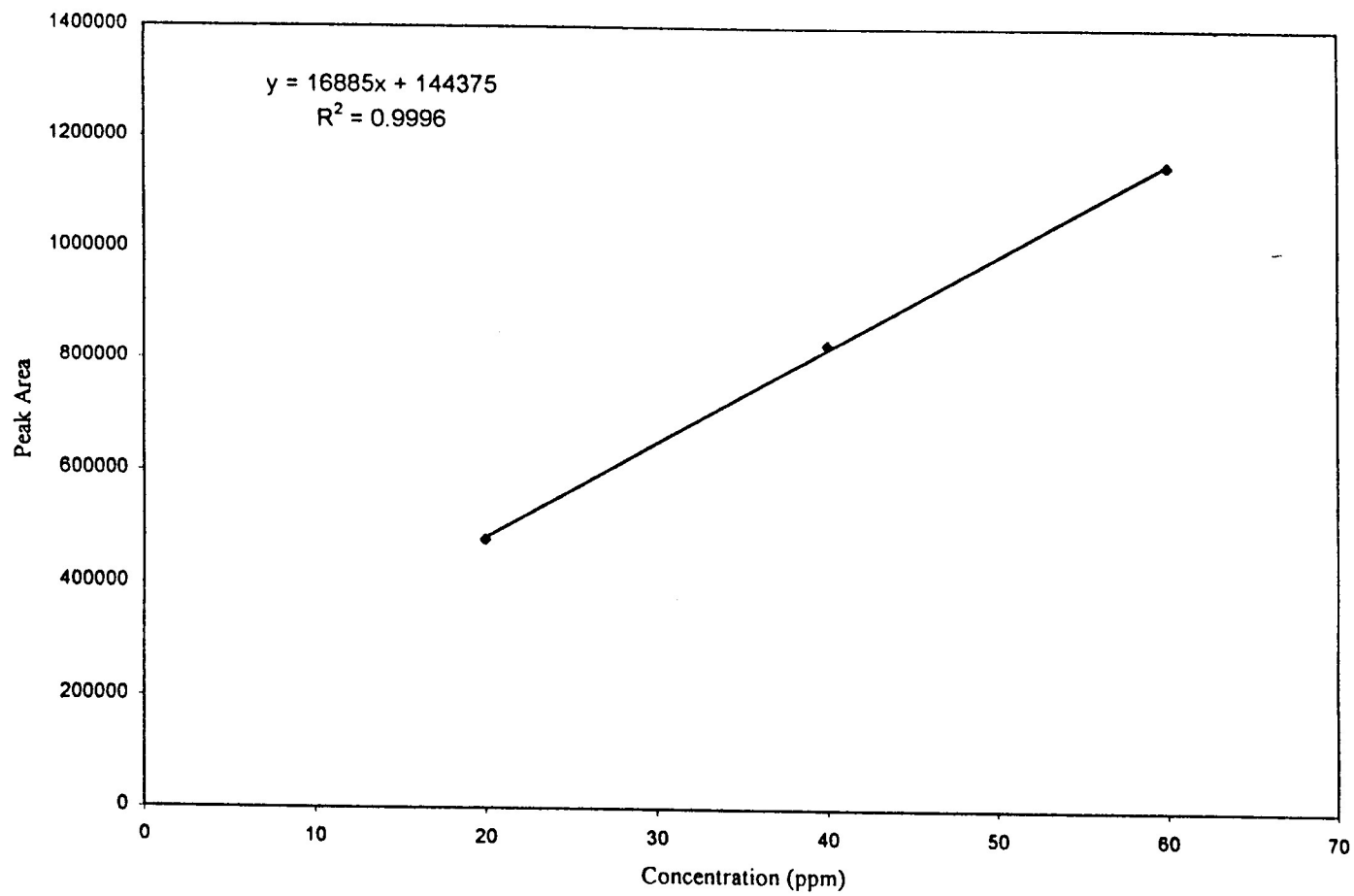


Figure 9. Calibration Curve for Fluorene by Injection (SIM)

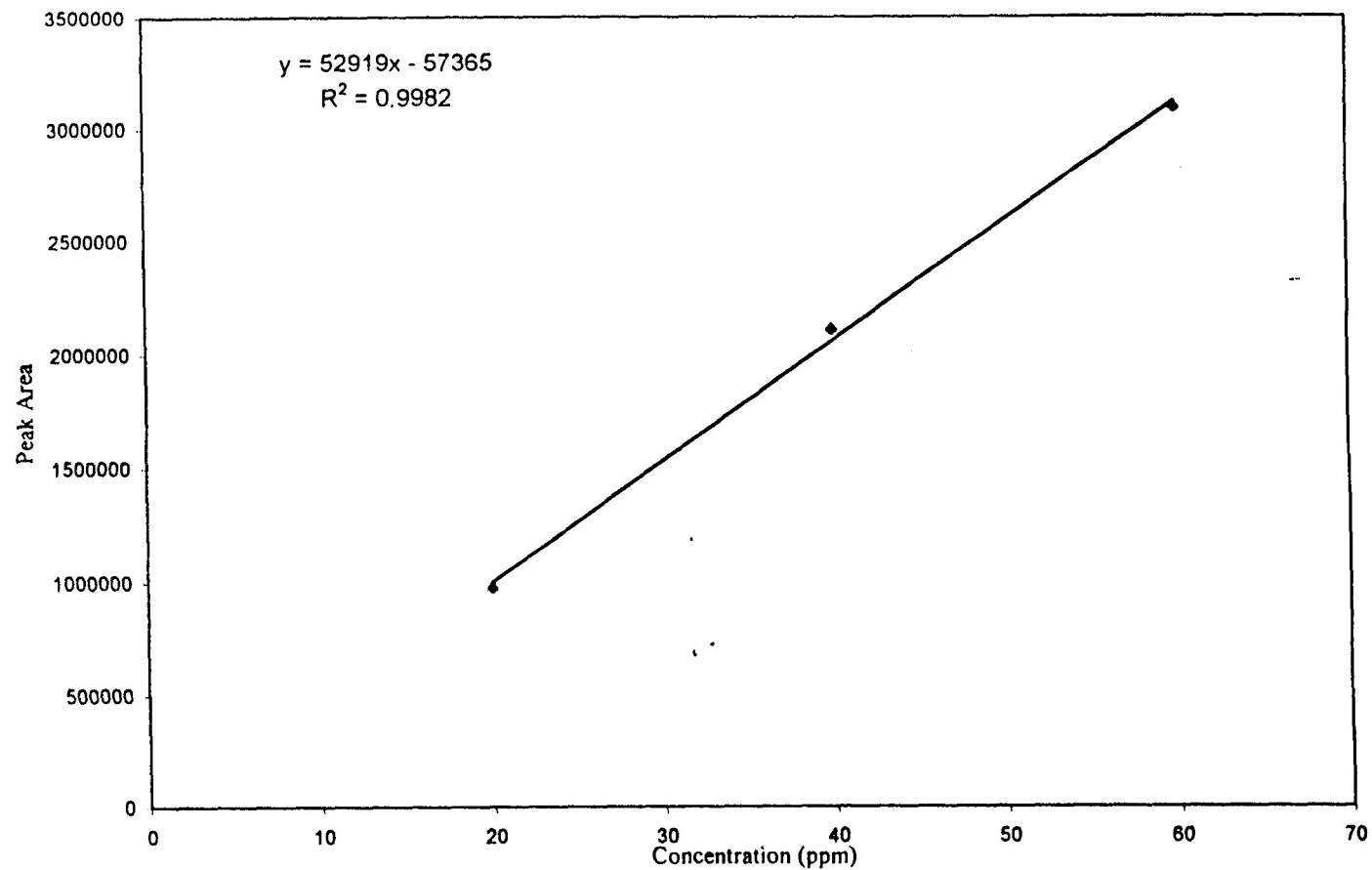


Figure 10. Calibration Curve for Naphthalene by Injection (SIM)

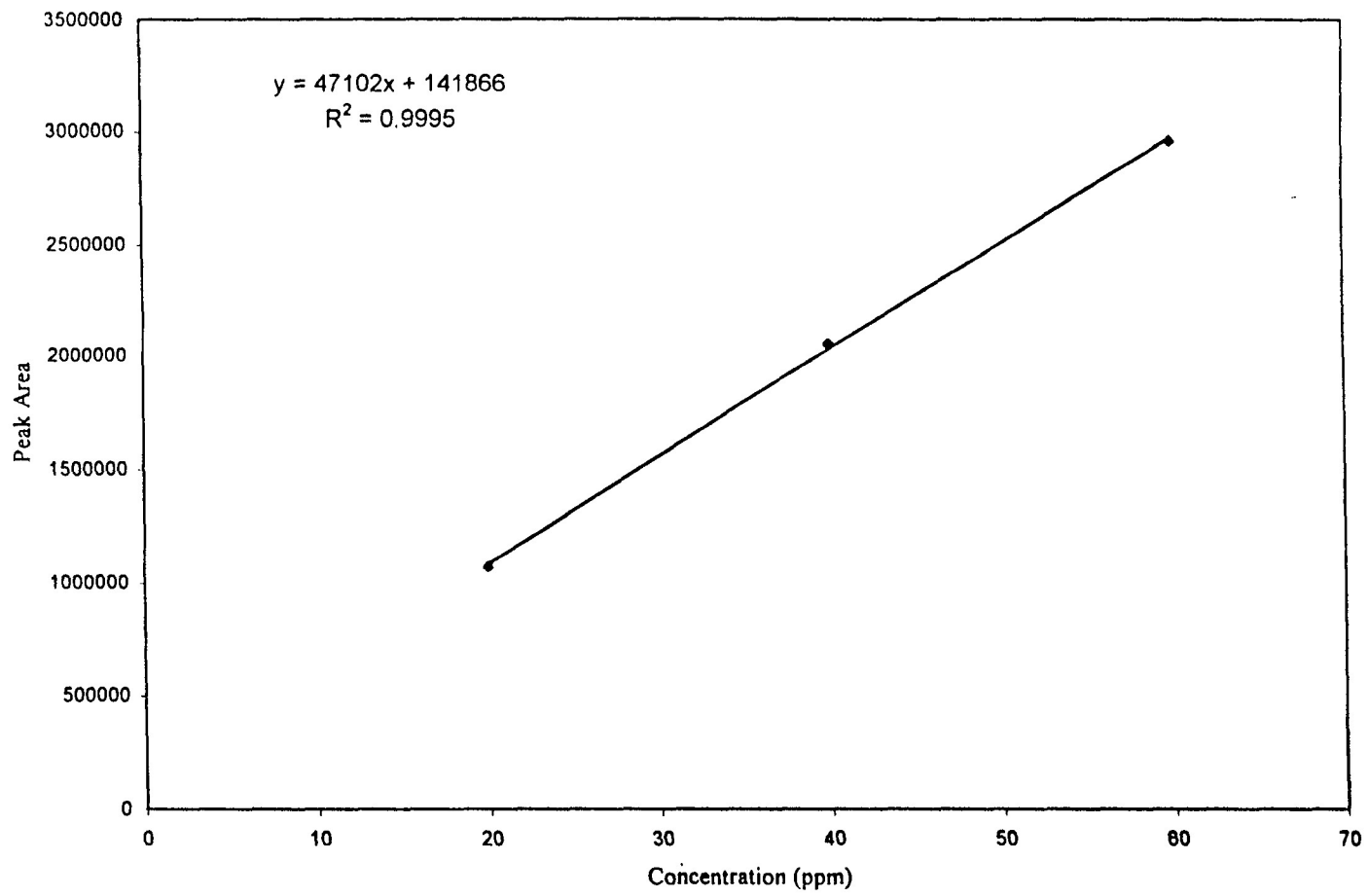


Figure 11. Calibration Curve for Acenaphthylene (SIM)

Table 20. Fluorene Standard On-Line (SIM)

<u>μg</u> <u>used</u>	<u>Peak #</u>	<u>Retention</u> <u>Time (min)</u>	<u>Area</u> <u>$\times 10^6$</u>	<u>Height</u> <u>$\times 10^6$</u>	<u>A/H(min)</u>
8 μg	6	24.9	0.25	0.02	15.99
5 μg	1	24.7	0.14	0.02	9.39
20 μg	1	24.9	3.30	0.15	21.38

The amount of fluorene used was 10 μL of 500 (5 μg), 10 μL of 2000 ppm (20 μg) and 200 μL of the 40 ppm (8 μg). Different amounts were used to find the detection limits for the standards. The detection limit for fluorene was found to be 6 μg . The percent recovery for fluorene was 0.26%. The detection limit was found by using smaller and smaller amounts of the sample until there was no sample detected using the method.

Table 21. Phenanthrene Standard On-Line (SIM)

<u>μg</u> <u>used</u>	<u>Peak #</u>	<u>Retention</u> <u>Time (min)</u>	<u>Area</u> <u>$\times 10^6$</u>	<u>Height</u> <u>$\times 10^6$</u>	<u>A/H(min)</u>
5 μg	1	29.5	0.01	0.01	5.31
5 μg	1	29.6	0.00	0.00	3.41

The amount of phenanthrene used for on-line analysis was 500 ppm, 10 μL (5 μg). The limit of detection for phenanthrene under these conditions was 5 μg . The recovery was 0.01%.

Table 22. Chrysene Standard On-Line (SIM)

<u>Conc.</u>	<u>Peak #</u>	<u>Retention Time (min)</u>	<u>Area x 10⁶</u>	<u>Height x 10⁶</u>	<u>A/H(min)</u>
500	*No Peak was found under these conditions.				
* This is thought to be due to the chrysene condensing on the heat transfer tube because of the high boiling point.					

Table 23. Naphthalene Standard On-Line (SIM)

<u>μg used</u>	<u>Peak #</u>	<u>Retention Time (min)</u>	<u>Area x 10⁶</u>	<u>Height x 10⁶</u>	<u>A/H(min)</u>
2 μg	1-4	15.5	0.00	0.00	2.90
8 μg	1-5	15.5	0.02	0.00	3.78
16 μg	1-5	15.5	0.06	0.01	4.60
24 μg	1-5	15.4	0.07	0.02	4.87

The percent recovery for this standard was 0.012%. The limit of detection for naphthalene using this method is 1 μg.

Table 24. Acenaphthylene Standard On-Line (SIM)

<u>μg</u> <u>used</u>	<u>Peak #</u>	<u>Retention</u> <u>Time (min)</u>	<u>Area</u> <u>$\times 10^6$</u>	<u>Height</u> <u>$\times 10^6$</u>	<u>A/H(min)</u>
2 μg	*No data exists for these conditions				
12 μg	1	21.9	0.01	0.00	5.93
24 μg	2	21.7	0.21	0.02	12.34

The amounts of acenaphthylene used were 2, 12, and 24 μg . This method gave a recovery of 0.055%. Under these conditions acenaphthylene was found to have a limit of detection of 2 μg .

IV. FURTHER STUDY

1. More analyses need to be performed using the on-line method to learn the problems with this method.
2. A different type of heat transfer line needs to be used when testing the on-line method to determine the type of line that will work with the different temperatures.
3. When the method is perfected organic samples from combustion in the AFBC system need to be analyzed on-line.

V. CONCLUSIONS

1. The on-line method of analysis was developed and tested.
2. PAH standards were analyzed by the on-line method, and the results were found to be comparable and similar to the data collected from injection of these standard PAHs.
3. Organic samples were analyzed using the GC-MS; these samples were collected on Tenax from the coal burning using the AFBC system. There were no PAHs or chlorobenzenes found to be present.

VI. BIBLIOGRAPHY

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