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QUARTERLY PROGRESS REPORT NO. 5
(October - December 1992)

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Contract No. DE-AC22-91-PC90366

on

CHARACTERIZATION OF AIR TOXICS FROM A
LABORATORY COAL-FIRED COMBUSTOR AND
UTILITY SCALE POWER PLANTS

to

PITTSBURGH ENERGY TECHNOLOGY CENTER
U.S. DEPARTMENT OF ENERGY
P.O. BOX 10940
PITTSBURGH, PENNSYLVANIA 15236

JANUARY 1993

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Columbus Operations
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Columbus Operations

January 1993

INTRODUCTION

This progress report summarizes technical accomplishments during the fourth quarter of 1992. The project began on September 25, 1991, and it is scheduled to conclude on November 30, 1993.

DESCRIPTION OF EXPERIMENTS

Laboratory combustor studies were conducted at Battelle to evaluate sampling methods and analysis techniques for air toxics generated by burning pulverized coal. The experimental setup is shown in Figure 1. Pulverized coal was burned in a series of eleven experiments as shown in Table 1. Coal was burned at two firing rates. In experiments 1-6 and 11, coal was burned at the "high" firing rate of 46 pounds per hour. In experiments 7-10, coal was burned at the low firing rate of 42 pounds per

Laboratory-Scale Combustion Facility

FIGURE 1

TABLE 1. LIST OF EXPERIMENTS

Experiment Number ^(a)	Date	O ₂ ^(b) , %	CO ₂ , %	CO, ppm	SO ₂ , ppm	NO _x , ppm	Temperature ^(c) , °F
0	10/06	5.4	8.5	36	142	99	285
1	10/07	4.9	13.5	53	1,500	371	279
2	10/08	5.0	13.3	72	1,520	381	278
3	10/09	5.0	13.7	67	1,360	338	288
4	10/10	5.1	13.8	67	1,370	417	302
5	10/12	5.2	14.0	77	1,330	422	298
6	10/14	5.5	13.1	55	1,370	417	297
7	10/15	5.4	13.3	68	1,610	438	281
8	10/16	5.3	13.5	68	1,550	474	279
9	10/17	5.6	14.8	68	1,590	530	271
10	10/18	5.3	14.1	80	1,590	395	267
11	10/19	5.2	13.9	85	1,530	435	280

(a) Experiment 0 was a baseline test burning natural gas. Coal was burned in experiments 1-11.

(b) Oxygen content in flue gas after addition of O₂/N₂ mixture.

(c) Temperature of flue gas at the point of sampling.

hour. Two coal firing rates were chosen to investigate whether or not the difference in combustion intensity (combustion temperature) has an effect on generation of air toxics.

This project is focussed on air toxics associated with fine particle fly ash. It is this size range of particles (less than about $7.5\ \mu\text{m}$ diameter) that are most relevant to questions concerning the influence of emitted fly ash on public health. From the outset, the U.S. Department of Energy (DOE) and Battelle and its subcontractor, Keystone/NEA, recognized that a key challenge was to collect sufficient quantity of particulate matter to identify and quantify air toxics species in samples, particularly organic compounds. For this reason, a goal of the combustor studies was to generate flyash and collect it from flue gases for at least 40 hours for each coal firing rate. In this time period Battelle hoped to collect a gram of material in each of three particle size ranges less than about $7.5\ \mu\text{m}$. These particle size ranges are listed in Table 2 for two types of sampling.

Samples were collected simultaneously by two methods. Samples were collected at flue gas temperature by the first method. Many air toxics species exist to a significant extent in both the gas and particle phases in the atmosphere. The distribution of their concentrations in the two phases depends upon temperature. When hot flue gases escape into the atmosphere they are cooled upon dilution and emitted vapors may adsorb onto the surface of fly ash particles thereby altering the phase distribution of the adsorbed species. Therefore, the second type of sampling consisted of simulating the plume processes of dilution and cooling in a Plume Simulating Dilution Sampler (PSDS). This provided the second type of samples listed in Table 2.

The Management Plan for this project calls for combining samples from daily experiments into four groups - hot flue gas and PSDS samples for both the high and low coal firing rates. Within each group will be three composite samples, one for each particle size range listed in Table 2. This approach was used to maximize the quantity of material for each analysis.

TABLE 2. PARTICLE SIZE RANGES FOR
COLLECTED PARTICULATE MATTER

Size Range Code ^(a)	Particle Size Range, μm	
	Hot Flue Samples	Plume Simulating Dilution Samples
A	3.2 - 6.8	3.5 - 7.5
B	0.88 - 3.2	0.86 - 3.5
C	<0.88	<0.86

(a) A denotes cyclone #2 with 50 percent particle diameter cut point of 3.2 and 3.5 μm for the hot flue and PSDS, respectively. A cyclone with a particle diameter cut point of 6.8 and 7.5 μm preceded cyclone #2 for the hot flue and PSDS, respectively.

B denotes cyclone #3 with diameter cut point of 0.88 and 0.86 μm for the hot flue and PSDS, respectively.

C denotes the filter following the cyclones.

COMBINATION OF SAMPLES FOR ANALYSIS OF
POLYCYCLIC AROMATIC HYDROCARBONS

Combination of samples for analysis began by evaluating the quantity of particulate matter collected by the three cyclones in both the hot flue sampling train and in the PSDS and the high volume quartz fiber filter in the PSDS. The smaller quartz filters in the hot flue gas train and also in the PSDS were not weighed for this decision on sample combination. They were used in the chemical analyses.

The quantity of particulate matter collected in each size range for each experiment is shown in Tables 3 and 4. The sample combination scheme is shown in Table 5. Note that samples from experiments 2-4 were not included in the composite samples for size ranges A-C in the HH composite samples (denoted as HHA, HHB, and HHC) and in size range C for sample HDC. Samples from experiments 3-5 were not included in size range A (from cyclone C2) for the HDA composite. This sample combination scheme was used because the cyclones became overloaded with particulate matter during a few of the experiments (the details of this occurrence are not discussed in this document).

The composite samples were extracted with two solvents: dichloromethane (DCM) and ethyl acetate (ETAC). The extracts correspond to material of a less polar (DCM) and more polar (ETAC) character. Table 6 contains the mass of extractable material for vapor samples (not the subject of this document) and the three particle size ranges. The DCM extracts have been analyzed for polycyclic aromatic hydrocarbons (PAH), and they will be analyzed for nitro-PAH, other target organic compounds and nontarget organic compounds (see page 33 of the Management Plan for a discussion of target and nontarget compounds). The PAH analyses for the DCM extract of XAD-2 samples were conducted following Procedure 01 described in the Appendix. The DCM extracts from hot-stack and diluted-stack fly ash samples were not fractionated, and the unfractionated DCM extracts were used for PAH analyses due to the small amount of extractable organic mass available in the DCM extracts. The ETAC extracts will be characterized for nontarget organic compounds. The significant aspect of the data in Table 6 for this document is the small quantity of extractable material in size ranges A

TABLE 3. QUANTITY OF PARTICULATE MATTER COLLECTED AT HIGH FIRING RATE IN THE LABORATORY COMBUSTOR EXPERIMENTS

Experiment Number	Date	Sampling Time, h	Quantity of Particulate Matter Collected, g ^(a)								
			HH ^(b)			HD ^(b)					
			C ₁	C ₂	C ₃	C ₁	C ₂	C ₃	Q		
0 (Gas)	10/06	8	-- ^(c)	--	--	--	--	--	--	--	--
1	10/07	5	2.153	3.491	0.752	1.132	0.104	0.012	0.187		
2	10/08	8	8.12 ^(d)	8.89 ^(d)	1.32 ^(d)	1.58 ^(d)	0.368	0.040	1.650		
3	10/09	8	8.36 ^(d)	7.77 ^(d)	1.23 ^(d)	1.76 ^(d)	0.633	0.043	2.746		
4	10/10	8	8.14 ^(d)	8.70 ^(d)	1.83 ^(d)	2.28 ^(d)	1.245	0.062	3.782		
5	10/12	5.5	0.597	3.025	0.666	0.181	2.735	0.025	0.809		
6	10/14	7.4	1.245	2.842	0.793	0.345	0.237	0.055	0.312		
11	10/19	7.2	0.719	1.979	0.682	0.172	0.146	0.038	0.282		

(a) Weights were measured in the laboratory.

(b) C₁-C₃ = Cyclones 1-3, Q = 8 x 10 in. quartz filter, HH denotes high firing rate and hot flue gas, HD denotes high firing rate and PSDS sampling.

(c) Not determined.

(d) Weights are approximate and were obtained in the field by Keystone/NEA to guide conduct of sampling.

TABLE 4. QUANTITY OF PARTICULATE MATTER COLLECTED AT LOW FIRING RATE IN THE LABORATORY COMBUSTOR EXPERIMENTS

Experiment Number	Date	Sampling Time, h	Quantity of Particulate Matter Collected, g ^(a)						
			LH ^(b)			LD ^(b)			
			C ₁	C ₂	C ₃	C ₁	C ₂	C ₃	Q
7	10/15	7	1.292	3.035	0.878	0.503	0.172	0.036	0.310
8	10/16	7	1.198	2.179	0.688	0.287	0.174	0.047	0.297
9	10/17	7.5	0.643	2.129	0.472	0.514	0.183	0.032	0.258
10	10/18	7	1.414	3.127	0.830	0.565	0.194	0.041	0.329

∞

(a) Weights were measured in the laboratory.

(b) C₁-C₃ = Cyclones 1-3, Q = 8 x 10 in. quartz filter, LH denotes low firing rate and hot flue gas, LD denotes low firing rate and PSDS sampling.

TABLE 5. COMBINATION SCHEME FOR SAMPLES

Coal Firing Rate	Particle Size Range	Composite Sample ID/Experiments Comprising Sample	
		Hot Flue Samples	PSDS Samples
High	A	HHA-1,5,6,11	HDA-1,2,6,11
	B	HHB-1,5,6,11	HDB-1-6,11
	C	HHC-1,5,6,11	HDC-1,5,6,11 ^(a)
Low	A	LHA-7,8,9,10	LDA-7,8,9,10
	B	LHB-7,8,9,10	LDB-7,8,9,10
	C	LHC-7,8,9,10	LDC-7,8,9,10

(a) The filter sample from experiment #11 was prepared and analyzed separately from the composite filter samples from experiments #1, #5, and #6, because field spiking was conducted for this filter sample (experiment #11).

TABLE 6. QUANTITY OF EXTRACTABLE MATTER IN SAMPLES COLLECTED DURING THE LABORATORY COMBUSTOR STUDIES

Coal Firing Rate	Type of Sample	Particle Size Range ^(b)	Hot-Stack Samples ^(c) (mg)		Diluted-Stack Samples (mg)	
			DCM	ETAC	DCM	ETAC
High	Vapor Particles ^(a)		13.5	-(d)	4.35	-
		A	1.36	1.00	0.88	0.52
		B	0.96	2.20	0.96	0.48
		C	0.64	1.08	9.68	185
Low	Vapor Particles		13.6	-	2.64	-
		A	1.44	1.24	0.48	1.00
		B	1.12	1.36	0.40	0.40
		C	0.48	37.6	8.32	225

(a) Samples collected in three particle diameter ranges.

(b) Size range codes A-C refer to the particle size ranges listed in Table 2.

(c) Extractable mass using two solvents: dichloromethane (DCM) and ethyl acetate (ETAC).

(d) Only DCM was used to extract vapor phase samples from the adsorbent.

and B for all 16 sample extracts and in size range C for three sample extracts. These small quantities of material suggest that there may be insufficient material in individual composite samples to characterize the samples for organic compounds.

The calculated mass concentration of particulate matter for individual samples is shown in Tables 7 and 8. The results for the PSDS samples are reported in their diluted state. Interpretation of these results is not provided in this document. The results are provided to illustrate of a mass concentration basis the quantities of fine particulate material in the experimental system.

RESULTS OF PAH ANALYSES

The results of the PAH analyses are shown in Tables 9-12 in terms of ng of material. The data in Tables 10 and 12 have not had the dilution factor of the PSDS applied to them. The nominal dilution rate was 27:1; Keystone/NEA is reducing the data now to calculate the actual dilution ratio for each experiment. The significant aspect of these data is the low values of PAH in terms of Battelle's ability to analyze the samples. Considering that nitro-PAH, for example, may only be at a tenth the concentration of the parent PAH there is very little material to work with.

PLANS FOR ANALYSIS OF TARGET AND NONTARGET ORGANIC COMPOUNDS

The remaining work to be done on the samples is analysis of the DCM extracts for target species and nontarget species and analysis of the ETAC extracts for nontarget species.

Hot Flue Samples HH and LH

In these samples the DCM extracts will be analyzed for nitrated-PAH target species (see Procedure 01 in the Appendix). Battelle recommends that the sample extracts for each particle size range A-C in samples HH and LH be analyzed

TABLE 7. MASS CONCENTRATIONS FOR SAMPLES COLLECTED AT HIGH FIRING RATE
IN THE LABORATORY COMBUSTOR EXPERIMENTS

Experiment Number	Hot Flue Samples ^(a) (mg/m ³)			PSDS Samples ^(a) (mg/m ³)			
	A	B	C		A	B	C
			T1	T2			
1	769	166	68.7	NA ^(b)	3.20	0.37	1.52
2	NA	NA	NA	NA	7.40	0.80	8.31
3	NA	NA	NA	NA	12.6	0.86	15.7
4	NA	NA	NA	NA	23.7	1.18	17.8
5	498	110	31.6	61.4	78.0	0.71	5.68
6	392	110	38.0	63.8	5.30	1.23	1.70
11	323	111	55.9	47.4	3.42	0.89	1.58

(a) A, B, and C denote the particle size ranges described in Table 2; T1 and T2 denote Teflon filter samples collected at different periods of each experiment; Q denotes quartz fiber filter sample (8 x 10) and T denotes Teflon filter samples.

(b) Samples whose mass concentrations are enclosed in boxes were not used to create composite samples. Those samples marked NA (not analyzed) were not weighed in the laboratory.

TABLE 8. MASS CONCENTRATIONS FOR SAMPLES COLLECTED AT LOW FIRING RATE
IN THE LABORATORY COMBUSTOR EXPERIMENTS

Experiment Number	Hot Flue Samples ^(a) (mg/m ³)				PSDS Samples ^(a) (mg/m ³)			
	A	B	C		A	B	C	
			T1	T2			Q	T
7	428	124	37.1	66.9	3.79	0.79	1.46	1.66
8	364	115	37.4	56.1	3.43	0.93	1.50	1.78
9	453	100	45.7	52.6	4.27	0.75	1.48	1.88
10	538	143	41.6	46.2	4.45	0.94	1.94	1.70

(a) A, B, and C denote the particle size ranges described in Table 2; T1 and T2 denote Teflon filter samples collected at different periods of each experiment; Q denotes quartz fiber filter sample (8 x 10) and T denotes Teflon filter samples.

TABLE 9. LEVELS OF POLYCYCLIC AROMATIC HYDROCARBONS, ng
IN HH SAMPLES

Compound	Particle Size Range			Total
	A	B	C	
Naphthalene	168	1790	167	2125
Biphenyl	9.83	11.3	12.2	33.3
Acenaphthylene	<5	<5	<5	<5
Acenaphthene	11.3	12.5	14.4	38.2
Fluorene	26.1	30.7	22.0	78.8
Phenanthrene	247	240	153	640
Anthracene	13.2	13.4	10.2	36.8
Fluoranthene	73.1	75.5	70.0	219
Pyrene	34.8	26.1	42.5	103
Benz[a]anthracene	<5	<5	5	5
Chrysene	<5	<5	<5	<5
Benzo[fluoranthene]	<5	<5	<5	<5
Benzo[e]pyrene	<5	<5	<5	<5
Benzo[a]pyrene	<5	<5	<5	<5
Indeno[1,2,3-c,d]pyrene	<5	<5	<5	<5
Benzo[g,h,i]perylene	<5	<5	<5	<5
Dibenzo[a,h]anthracene	<5	<5	<5	<5
Coronene	<5	<5	<5	<5
Dibenzo[a,l]pyrene	<5	<5	<5	<5
Dibenzo[a,e]pyrene	<5	<5	<5	<5
Dibenzo[a,h]pyrene	<5	<5	<5	<5

TABLE 10. LEVELS OF POLYCYCLIC AROMATIC HYDROCARBONS, ng
IN HD SAMPLES^(a)

Compound	Particle Size Range			Total
	A	B	C	
Naphthalene	151	98.4	202	451
Biphenyl	27.1	11.7	1670	1710
Acenaphthylene	67.8	29.8	54.0	152
Acenaphthene	23.7	19.4	99.0	142
Fluorene	144	64.6	121	330
Phenanthrene	566	397	1150	2110
Anthracene	39.0	36.9	54.0	130
Fluoranthene	249	304	639	1190
Pyrene	110	135	166	411
Benz[a]anthracene	7.46	19.4	13.9	40.8
Chrysene	6.95	15.7	18.0	40.7
Benzofluoranthenes	<5	16.3	5.40	21.7
Benzo[e]pyrene	<5	13.8	13.0	26.8
Benzo[a]pyrene	<5	<5	<5	<5
Indeno[1,2,3-c,d]pyrene	<5	10.4	<5	10.4
Benzo[g,h,i]perylene	<5	16.0	<5	16.0
Dibenzo[a,h]anthracene	<5	<5	<5	<5
Coronene	<5	<5	<5	<5
Dibenzo[a,l]pyrene	<5	<5	<5	<5
Dibenzo[a,e]pyrene	<5	<5	<5	<5
Dibenzo[a,h]pyrene	<5	<5	<5	<5

(a) Data are not corrected for dilution factor.

TABLE 11. LEVELS OF POLYCYCLIC AROMATIC HYDROCARBONS, ng
IN LH SAMPLES

Compound	Particle Size Range			Total
	A	B	C	
Naphthalene	83.3	69.4	31.8	184
Biphenyl	31.2	15.8	31.1	78.1
Acenaphthylene	<5	5.0	<5	5.0
Acenaphthene	15.6	19.1	14.0	48.7
Fluorene	26.9	32.3	20.5	79.7
Phenanthrene	93.0	162	146	401
Anthracene	5.0	6.84	10.4	22.2
Fluoranthene	23.8	41.3	74.8	140
Pyrene	9.68	16.8	16.7	43.2
Benz[a]anthracene	<5	<5	8.02	8.02
Chrysene	<5	<5	5.58	5.58
Benzo[fluoranthene]	<5	<5	<5	<5
Benzo[e]pyrene	<5	<5	<5	<5
Benzo[a]pyrene	<5	<5	<5	<5
Indeno[1,2,3-c,d]pyrene	<5	<5	<5	<5
Benzo[g,h,i]perylene	<5	<5	<5	<5
Dibenzo[a,h]anthracene	<5	<5	<5	<5
Coronene	<5	<5	<5	<5
Dibenzo[a,l]pyrene	<5	<5	<5	<5
Dibenzo[a,e]pyrene	<5	<5	<5	<5
Dibenzo[a,h]pyrene	<5	<5	<5	<5

TABLE 12. LEVELS OF POLYCYCLIC AROMATIC HYDROCARBONS, ng,
IN LD SAMPLES^(a)

Compound	Particle Size Range			Total
	A	B	C	
Naphthalene	60.3	49.3	611	721
Biphenyl	47.5	10.0	397	454
Acenaphthylene	71.2	14.8	535	621
Acenaphthene	27.4	16.8	65.0	109
Fluorene	217	53.0	1120	1390
Phenanthrene	384	241	2050	2680
Anthracene	29.2	20.1	138	187
Fluoranthene	126	117	359	602
Pyrene	47.5	38.4	160	246
Benz[a]anthracene	<5	<5	9.9	9.9
Chrysene	<5	<5	13.8	13.8
Benzo[a]fluoranthene	<5	<5	<5	<5
Benzo[e]pyrene	<5	<5	<5	<5
Benzo[a]pyrene	<5	<5	<5	<5
Indeno[1,2,3-c,d]pyrene	<5	<5	<5	<5
Benzo[g,h,i]perylene	<5	<5	<5	<5
Dibenzo[a,h]anthracene	<5	<5	<5	<5
Coronene	<5	<5	<5	<5
Dibenzo[a,l]pyrene	<5	<5	<5	<5
Dibenzo[a,e]pyrene	<5	<5	<5	<5
Dibenzo[a,h]pyrene	<5	<5	<5	<5

(a) Data are not corrected for dilution factor.

separately. The ETAC extracts will not be analyzed for these samples in accordance with the Management Plan.

PSDS Samples HD and LD

The target species to be analyzed in the DCM extracts are nitrated-PAH, hydroxylated-NO₂-aromatic PAH (OH-NO₂-AR/PAH), and PAH derivatives containing either a sulfur (PASH), nitrogen (PANH) or oxygen (oxy-PAH) (see Procedure 02 in the Appendix). Battelle recommends that extracts from particle size ranges A and B for both HD and LD samples be combined together for analysis. This combination will provide a sample quantity of 2.73 mg (0.88 + 0.96 + 0.48 + 0.40, from Table 6) to begin the fractionation into polarity classes.

By combining the extracts in this manner it will not be possible to develop data differentiated by (1) particle size within the two size classes or 2) coal firing rate. The overriding factor, in Battelle's opinion, is that without combining the four extracts into one, it is likely that measurements of most of the target species will result primarily in nondetectable results because of the small concentrations of these species in the samples combined with the small quantity of sample. Battelle believes that it is most important to obtain measurable results for the species to guide the planning effort for the power plant study in the summer of 1993. The best opportunity to accomplish this goal for these difficult to measure species is by working with as much material as possible.

Two other considerations are that there will still be differentiation of results by particle size for size range C versus the combined A+B. Also, results for PAH and other analytes (not reported herein) suggest that the differences in samples between the two coal firing rates may not be significant. Both of these considerations support Battelle's recommendation to combine the extracts according to the scheme cited above.

The nontarget species to be analyzed in the DCM and ETAC extracts are listed in Figure 1 of Procedure 02. Because the same DCM extracts will be fractionated and then analyzed for both target and nontarget species, the nontarget analyses of DCM extracts must be on a combined extract if that is done for the target species. For the reasons cited above, Battelle recommends that the ETAC extracts from size ranges A

and B be combined into one composite. From Table 6, this will provide 2.4 mg of material to work with.

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