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Research Triangle Park NC 27711

EMB Report 79-CKO-17
September 1979

Air

EPA

Iron and Steel (Coke Oven Battery Stack)

Emission Test Report Jones & Laughlin Steel Corporation Pittsburgh, Pennsylvania

BY-PRODUCT COKE PLANT
BATTERY P4

Jones and Laughlin Steel Corporation
Pittsburgh, Pennsylvania

Prepared for the

U.S. Environmental Protection Agency
Emission Measurement Branch
Research Triangle Park, North Carolina 27711

Prepared and compiled by

Clayton Environmental Consultants, Inc.
25711 Southfield Road
Southfield, Michigan 48075

EMB REPORT NO. 79-CKO-17

Work Assignment 14

Contract No. 68-02-2817

INTRODUCTION TO REPORT

Two firms prepared this report under contract to the U. S. Environmental Protection Agency. The report is presented in two sections. Section I was prepared by Clayton Environmental Consultants, Inc., Southfield, Michigan and includes test results for particulate, carbon monoxide, carbon dioxide, oxygen, and benzene, as well as visible emission data. Section II was prepared by TRW Energy Systems Group, Durham, North Carolina, and contains benzo(a)pyrene (B(a)P) sampling data only, and immediately follows Appendix I of the Clayton report.

TRW did all B(a)P sampling for this study and four other studies conducted for this coke oven battery stack series. At the time the initial work assignments were issued, TRW was the only contractor suitably equipped for B(a)P sampling.

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1.0 INTRODUCTION

The U.S. Environmental Protection Agency (EPA) retained Clayton Environmental Consultants, Inc. to determine various gas and particulate emissions from the P4 coke oven battery stack at the Jones and Laughlin Steel Corporation, Pittsburgh Coke Works, in Pittsburgh, Pennsylvania. The results of this study will be used in research and development efforts for supporting New Source Performance Standards for coke oven battery stacks in the iron and steel industry. This study was commissioned as EMB Project No. 79-CKO-17, Contract No. 68-02-2817, Work Assignment 14.

The testing program included the following:

(1) triplicate samples of particulate matter;

(2) integrated bag samples for benzene and Orsat analyses;

(3) continuous carbon monoxide measurement during the particulate runs (EPA Method 10, NDIR analyzer);

(4) sulfate analysis of the particulate samples; and,

(5) visible emission observations recorded for the duration of each particulate sample run.

Auxiliary data included exhaust gas velocities, temperatures, and flowrates as determined from the traverses. Figure 1.1 presents a schematic of the process/control system layout as tested.

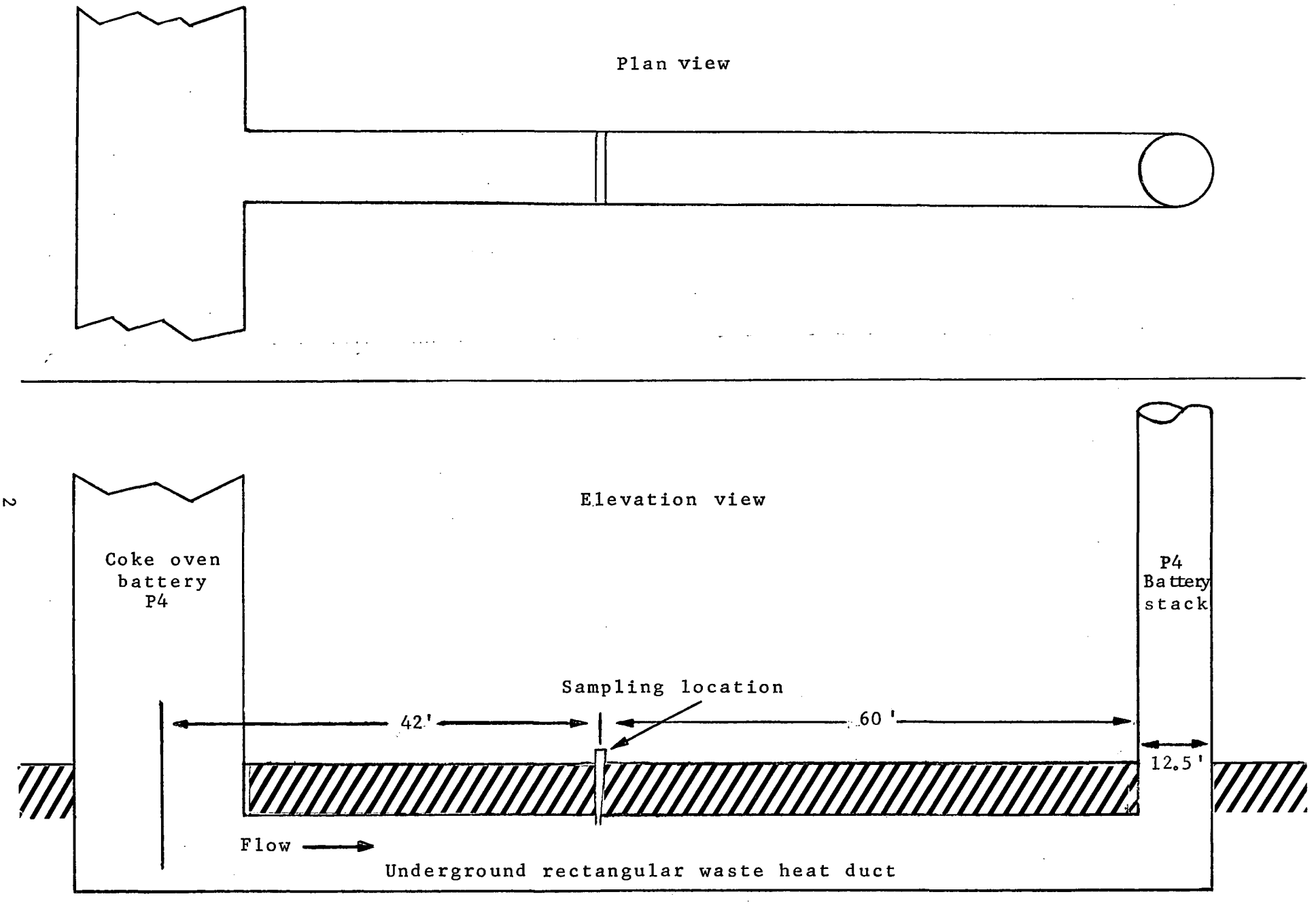


Figure 1.1. Process layout - waste heat flue duct.

2.0 SUMMARY AND DISCUSSION OF RESULTS

PARTICULATE EMISSIONS

Results of the particulate emission study are presented in Tables 2.1, 2.2, and 2.3. Tables 2.1 and 2.2 present the concentrations and emission rates of filterable and total particulate and sulfate, respectively. Concentrations are expressed as grains per dry standard cubic foot (gr/dscf) and milligrams per dry standard cubic meter (mg/dscm). Emission rates are expressed as pounds per hour (lb/hr) and kilograms per hour (kg/hr). Table 2.3 presents sulfate as a percent by weight of filterable and total particulate. Averages are presented for each sample run in all three tables.

Table 2.1 indicates the measured filterable concentrations of particulate in the waste heat duct ranged from 0.195 to 0.286 gr/dscf (446 to 655 mg/dscm) and averaged 0.234 gr/dscf (535 mg/dscm). Concentrations of total particulate ranged from 0.362 to 0.370 gr/dscf (829 to 847 mg/dscm) and averaged 0.365 gr/dscf (837 mg/dscm). Emission rates for filterable particulate ranged from 74.6 to 116 lb/hr (33.9 to 52.6 kg/hr) and averaged 89.3 lb/hr (40.5 kg/hr). Total particulate emission rates ranged from 123 to 150 lb/hr (55.6 to 68.1 kg/hr) and averaged 139 lb/hr (63.0 kg/hr).

TABLE 2.1. PARTICULATE CONCENTRATIONS AND EMISSION RATES
P4 BATTERY WASTE HEAT DUCT

Sample Number	Sample Date	Stack Gas Parameters		Concentration				Emission Rate			
		Flowrate	Temp	Filterable		Total		Filterable		Total	
		dscfm	F	gr/dscf	mg/dscm	gr/dscf	mg/dscm	lb/hr	kg/hr	lb/hr	kg/hr
1	5/1/79	46,200	599	0.195	446	0.364	834	77.2	35.0	144	65.4
2	5/2/79	39,500	603	0.220	505	0.362	829	74.6	33.9	123	55.6
3	5/3/79	47,300	604	0.286	655	0.370	847	116	52.6	150	68.1
Average		44,300	602	0.234	535	0.365	837	89.3	40.5	139	63.0

Total Particulate = Front half (filterable) + Back half.

Front Half = nozzle, probe, filter, and front half of filter holder.

Back Half = back half of filter holder, flexline, impingers, and connectors.

Filterable concentrations of sulfate (Table 2.2) ranged from 0.100 to 0.141 gr/dscf (228 to 324 mg/dscm) and averaged 0.117 gr/dscf (268 mg/dscm). Total sulfate concentrations ranged from 0.228 to 0.242 gr/dscf (522 to 554 mg/dscm) and averaged 0.235 gr/dscf (538 mg/dscm). Emission rates ranged from 37.2 to 57.3 lb/hr (16.9 to 26.0 kg/hr) for filterable sulfate and averaged 44.7 lb/hr (20.3 kg/hr). Total sulfate emission rates ranged from 79.8 to 95.8 lb/hr (36.2 to 43.4 kg/hr) and averaged 89.4 lb/hr (40.5 kg/hr). Table 2.3 indicates that sulfate as a percent by weight of filterable particulate ranged from 49.4 to 51.2 percent and averaged 50.1 percent. Sulfate as a percent by weight of total particulate ranged from 61.6 to 66.4 percent and averaged 64.4 percent.

Sulfate represents the major constituent of the filterable and total particulate fractions. This indicates that by reducing the sulfur content of the coke oven gas, the particulate concentrations should correspondingly drop. The planned gas desulfurization is, therefore, a noteworthy addition.

The general reproducibility of the particulate emission data collected for all three sample runs was good although magnitudes were somewhat higher than expected. Previous testing on Battery P4 had indicated an average

TABLE 2.2. SULFATE CONCENTRATIONS AND EMISSION RATES
P4 BATTERY WASTE HEAT DUCT

Sample Number	Sample Date	Stack Gas Parameters		Concentration				Emission Rate			
		Flowrate	Temp	Filterable		Total		Filterable		Total	
		dscfm	F	gr/dscf	mg/dscm	gr/dscf	mg/dscm	lb/hr	kg/hr	lb/hr	kg/hr
1	5/1/79	46,200	599	0.100	228	0.242	554	39.5	17.9	95.8	43.4
2	5/2/79	39,500	603	0.110	251	0.236	539	37.2	16.9	79.8	36.2
3	5/3/79	47,300	604	0.141	324	0.228	522	57.3	26.0	92.5	41.9
Average		44,300	602	0.117	268	0.235	538	44.7	20.3	89.4	40.5

Total Particulate = Front half (filterable) + Back half.

Front Half = nozzle, probe, filter, and front half of filter holder.

Back Half = back half of filter holder, flexline, impingers, and connectors.

TABLE 2.3. SULFATE AS PERCENT OF PARTICULATE BY WEIGHT

Sample Number	Filterable Percent	Total Percent
1	51.2	66.4
2	49.8	65.1
3	49.4	61.6
Average	50.1	64.4

filterable particulate concentration of 0.090[a] gr/dscf, 61.5 percent lower than this test series. These previous tests were performed at a less than ideal location. The heat canal was accessed through four randomly spaced ports. This random spacing did not permit sampling to be performed in accordance with Method 1 specifications for sample and velocity traverses of stationary sources. For this reason, the validity of the data from the previous testing program may be questionable.

The heat canal, for this study, was accessed through ports located in the top of a vertical cut-off damper slot. The location of these ports was in accordance with Method 1. Since the slot tapered towards the bottom, the possibility existed of accidentally picking up material by scraping the nozzle on the walls of the slot, as the probe was being raised or lowered through a port. This would have biased the sample values toward the high side. It is therefore unlikely that any random scraping was influential, since the test results are consistent and reproducible.

BENZENE EMISSIONS

Results of the benzene analyses are presented in Table 2.4. Benzene concentrations ranged from 0.6 to 1.6 ppm and averaged 1.1 ppm. Emission rates ranged

[a] An average of 10 runs from a study conducted in April, 1975 by Betz Environmental.

TABLE 2.4. BENZENE CONCENTRATIONS AND EMISSION RATES

Sampling Location	Sample Number	Sample Date	Concentration	Emission Rate	
			ppm	lb/hr	kg/hr
P4 Battery Stack	1	5/1/79	0.6	0.3	0.1
	2	5/2/79	1.6	0.6	0.3
	3	5/3/79	1.1	0.5	0.2
	Average		1.1	0.5	0.2

from 0.3 to 0.6 lb/hr (0.1 to 0.3 kg/hr) and averaged 0.5 lb/hr (0.2 kg/hr). These results show a high degree of reproducibility, although they are lower than had been anticipated.

EXHAUST GAS COMPOSITION

Table 2.5 displays the results of the exhaust gas composition analysis. Determinations of carbon dioxide, oxygen, and carbon monoxide contents were made for each of the three sample runs. Moisture content is also presented and shows an average of 16.0-percent. The initial gas composition sample was voided due to a leaky bag. The results of Sample Nos. 2 and 3 were averaged and these averages were used for Sample No. 1 determination.

VISIBLE AND CARBON MONOXIDE EMISSIONS

Visible emissions from the coke oven Battery P4 stack were recorded for the duration of each particulate sample run, except Run No. 3, for which visible emissions were abbreviated due to inclement weather. The observations were performed in accordance with EPA Method 9 by a qualified visible emissions observer. A graphic summary of opacities is presented in Figures 2.1, 2.2, and 2.3. Additional visible emission data is

TABLE 2.5. EXHAUST GAS COMPOSITION - P4 BATTERY WASTE HEAT DUCT

Sample Number	Moisture Content Percent	Exhaust Gas Composition, Dry Basis Percent			
		Carbon Dioxide	Oxygen	Carbon Monoxide	Nitrogen and Inerts
1	16.3	3.6[a]	11.6[a]	0.2[a]	84.6
2	16.0	4.0	10.6	<0.1	85.4
3	15.6	3.1	12.5	0.3	84.1
Average	16.0	3.6	11.6	0.2	84.7

[a] Sample 1 was voided due to a leaky bag and an average of Samples 2 and 3 was used.

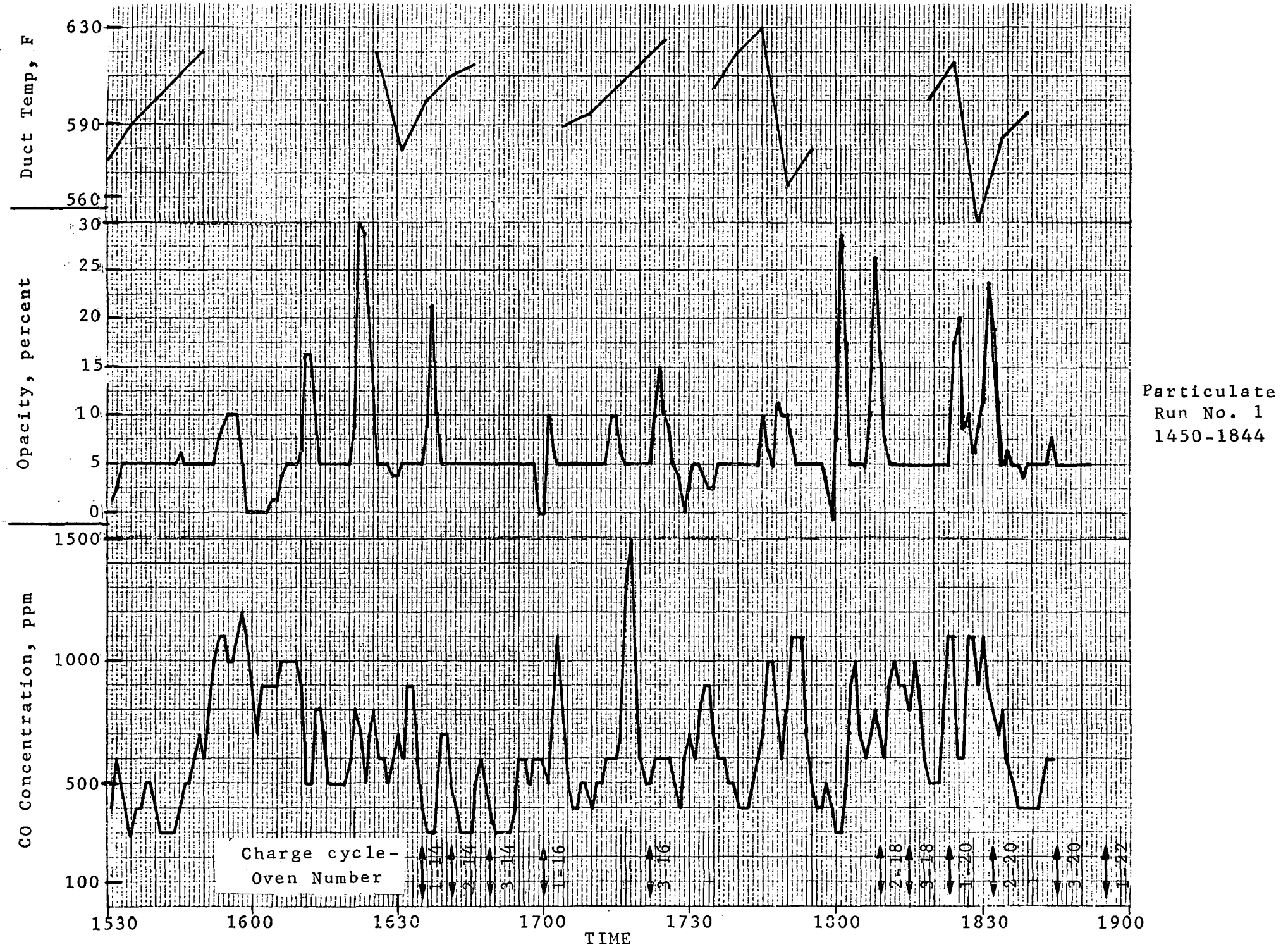
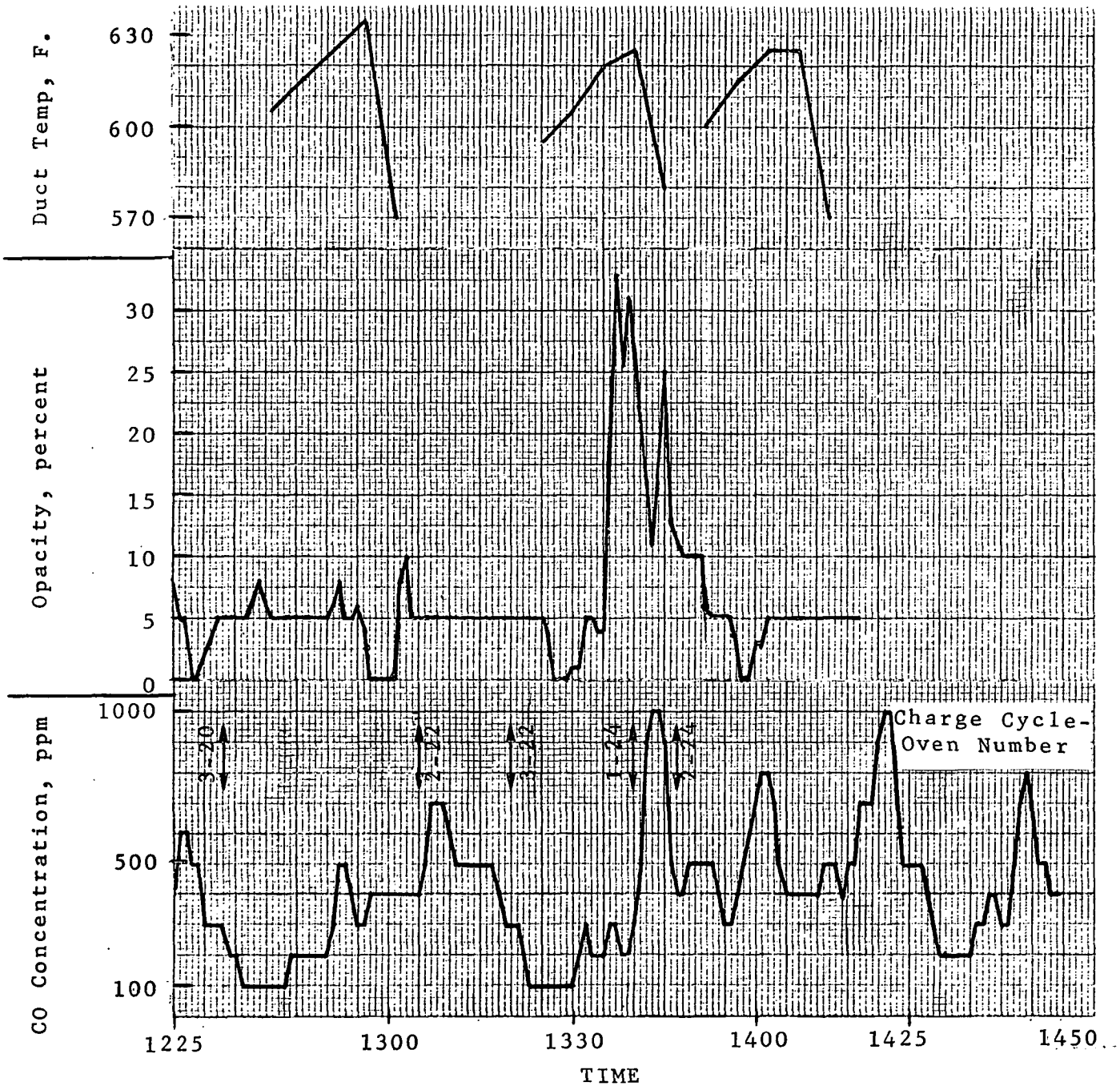


Figure 2.1. Relationship of CO concentrations, stack opacity, and duct temperature.



Particulate
Run No. 2
1045-1407

Figure 2.2. Relationship of CO Concentrations, stack opacity, and duct temperature.

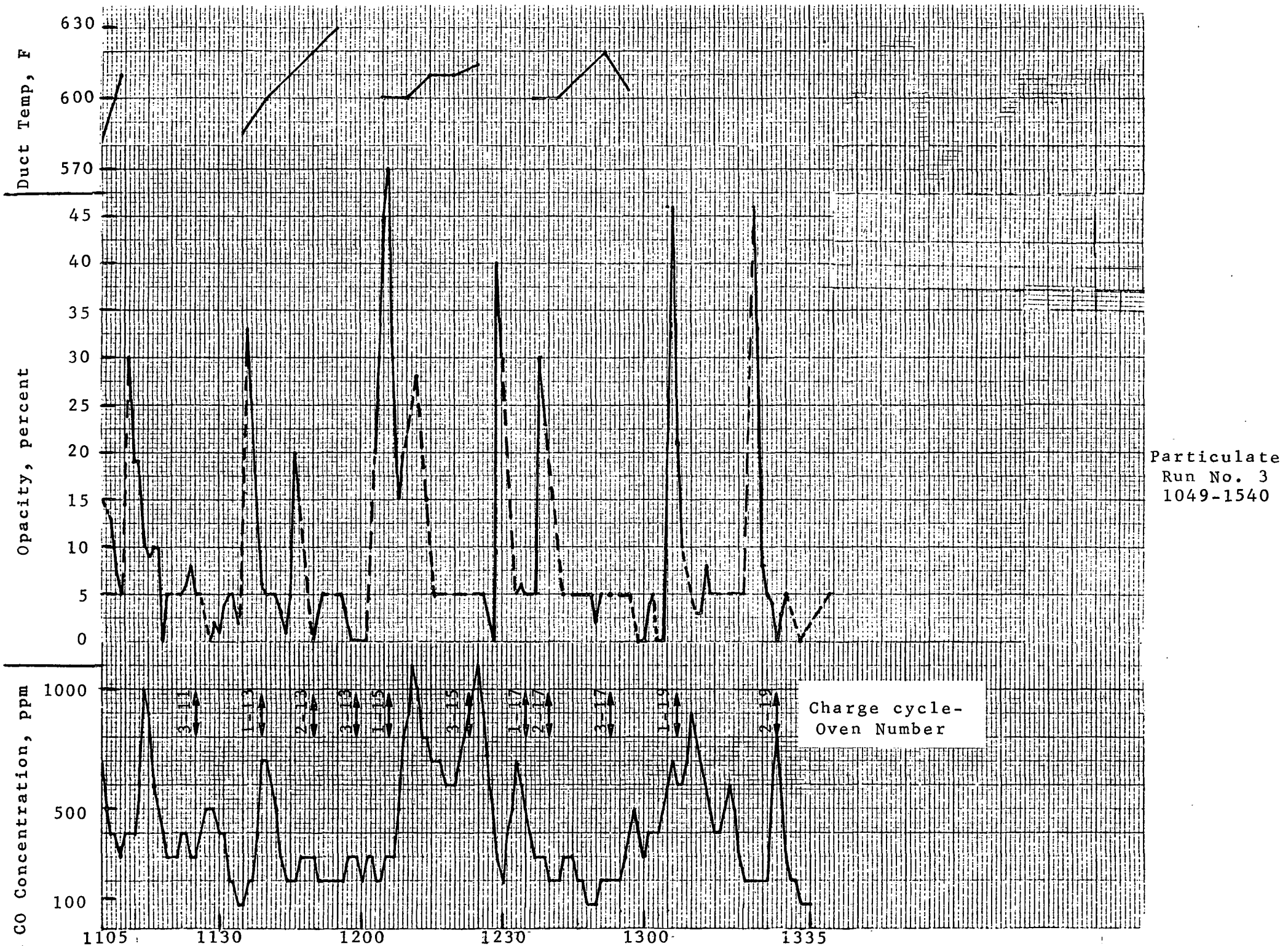


Figure 2 3 Relationship of CO Concentrations stack opacity, and duct temperature

included in Appendix B. Carbon monoxide concentrations are also plotted on Figures 2.1, 2.2, and 2.3.

Correlations seemed to exist between the continuously monitored concentrations of carbon monoxide (ppm), the actual charging operation of individual coke ovens (oven charges indicated by a vertical line above the axis), and opacity; thus, a linear regression and correlation analysis was performed on the data. Based on these statistical results, further statistical analyses of the data would be conducted if such information seemed beneficial to a better interpretation of the data. The following presents the methodology and results of these statistical analyses.

General Procedures

The time-concentration curves were reduced in the following manner: The carbon monoxide strip chart continuous readings were reduced to individual 15-second average concentrations to correspond with discrete 15-second opacity readings. A data file was then created which included time and each corresponding opacity and CO reading at that time. One such data file was created for each sample run.

Since subjective observations indicated that CO concentration peaks were generally preceded within a few minutes by a rise in opacity, a computer program was devised which would accommodate and adjust the data set pairings to any given lag time. The lag time

indicates the time, in minutes, before or after (negative or positive) the opacity for the associated CO reading. Each data file was then run through a linear regression program and correlation routine to determine if a valid relationship existed between the data for any given lag time. Different lag times (positive and negative) were used in determining the maximum correlation coefficient, beginning at whole minute intervals, then reducing it to quarter-minute intervals. This usually required five to ten runs per sample.

Several problems necessitated altering the data inputs to accommodate a more realistic analysis. For example, steam exiting the quench tower occasionally obscured the battery stack emissions. Therefore, for these points in time, there would be associated CO readings but no opacity readings. Thus, these data could not be counted as a valid data set. The number of complete pairs of data available for correlation then, i.e., the number of data sets used, was less than the total number of pairs first described (above). Therefore, a new data file was created based on the optimum time lag, using only complete data sets in the subsequent analysis.

Results

Table 2.6 presents the results of the correlation analyses. Each run showed an optimum lag time to produce a maximum correlation coefficient (r) which varied from

TABLE 2.6. SUMMARY OF CORRELATION RESULTS

Sample Number	Number of Data Sets	% of Data Used	Correlation Coefficient (r)	Linear Regression Equation	Lag Time,[a] Minutes
	810	100[b]	0.23	CO = 11.1 op + 570	
1		89.0	0.33	CO = 13.3 op + 505	2.5
		86.5	0.33	CO = 14.0 op + 497	
	478	100[b]	0.52	CO = 16.0 op + 270	
2		92.1	0.65	CO = 17.8 op + 226	5
		79.9	0.75	CO = 20.5 op + 176	
	394	100[b]	0.55	CO = 10.6 op + 298	
3		95.7	0.64	CO = 11.3 op + 270	4
		85.3	0.73	CO = 12.6 op + 227	

[a]Minutes from opacity reading to the carbon monoxide reading.

[b]100% of data implies total number of data sets. Other values are percentages of this number.

2.5 to 5 minutes. Using 100-percent of the data produced an r value of 0.55 or less for each sample. This may or may not be relevant, but does suggest that there could be factors affecting opacity other than CO and factors affecting CO other than opacity which may independently affect the results, in addition to any relationship shown to exist between CO and opacity.

The computer outputs also included a table showing the data distribution (Appendix E-2). Using the distribution and the file of correlated data points, it may be seen which pairs were most likely affected by other variables (i.e., the outliers on the distribution). Without sufficient operations data to interpret what other variables were affecting the distribution, it was impossible to logically eliminate outlying points. Therefore, certain data pairings were eliminated from further computer runs according to the following methodology: When CO readings were high (i.e., 500 ppm) during periods of low opacity (i.e., 0-percent), it was intuitively apparent that factors affecting CO levels were probably not affecting opacity at that time. Therefore, a certain percentage of data sets were deleted and the correlation analysis rerun using the same optimum lag time. This reduced the total data

sets considered (shown on Table 2.6 as a percentage of the total) and increased the correlation coefficient in each case.

In Samples 2 and 3, the r value was 0.7 using about 80-percent of the data. The r value from Sample 1 was extremely low (i.e., 0.23) using 100-percent of the data. Upon examination of the data distribution it was discovered that 72-percent of the opacity readings were 5-percent, showing very little relationship at all with CO readings.

In the next step, an additional variable, oven charge time, was introduced into the data file to further investigate the relationship of CO and opacity. The times of oven charging were marked with a "C" within the original data file. The program was structured to utilize various intervals around the charge period. The correlation analysis was then rerun based on the optimum time lag as determined from the first set of runs (Table 2.6).

The results are presented in Table 2.7. Optimum charge intervals varied from 0.25 to 2.75 minutes. Sample 3 was run at two intervals surrounding the charging activity, examining the paired CO and opacity data at both 15-seconds and 60-seconds before and after the charge. Samples 1 and 2 were based on 1.0 and 2.75

TABLE 2.7. CO AND OPACITY CORRELATION CONSIDERING OVEN CHARGE TIMES

Sample Number	Charge Interval, Minutes	Number of Data Sets	% of Data Used	Correlation Coefficient (r)	Linear Regression Equation	Lag Time,[a] Minutes
1	1	90	100[b]	0.48	CO = 21.0 op + 461	2.5
			94.4	0.47	CO = 22.6 op + 454	
			90.0	0.61	CO = 29.2 op + 377	
			76.7	0.74	CO = 27.6 op + 324	
2	2.75	112	100[b]	0.75	CO = 24.9 op + 160	5
			79.5	0.92	CO = 30.0 op + 19.3	
3	1	59	100[b]	0.78	CO = 12.3 op + 320	4
			84.8	0.88	CO = 13.6 op + 264	
	0.25	20	100[b]	0.90	CO = 15.2 op + 301	
			85.0	0.93	CO = 16.0 op + 270	

[a]Minutes from opacity reading to the carbon monoxide reading.

[b]100% of data implies total number of data sets. Other values are percentages of this number.

minute intervals surrounding the charge, respectively. Samples 2 and 3 (at the 1.0 minute interval) had correlation coefficients of 0.75 and 0.78, respectively. By reducing total data pairs to 79.5 and 84.8-percent, respectively, the same samples had respective correlation coefficients of 0.92 and 0.88. Sample 1 was again lowest with a coefficient of 0.48 based on 100-percent of the data, and 0.74 using 76.7-percent of the data.

Based on the results of Sample Nos. 2 and 3, for 80 percent of the time there is good correlation between opacity and carbon monoxide during the charge intervals. Additional information would be needed to validate this relationship, such as the occurrence of extraneous factors which influence either opacity or carbon monoxide, when these factors occur, and the magnitude of these influences. With this information, any given charge interval could be assessed for its independence from other factors, such as topside explosions and fires, which could then be isolated and rationally removed from the carbon monoxide and opacity data. The data used in the correlation analysis would then be more qualified and the correlation coefficient would be more meaningful. With this approach to the analysis, the correlation is both quantitative and qualitative. Based on the number of data pairs used, opacity and carbon monoxide can be related quantitatively over a percentage of time and the resulting correlation coefficient would indicate the quality of the relationship.

3.0 PROCESS DESCRIPTION AND OPERATION (supplied by Midwest Research Institute)

There are five coke oven batteries at the Jones and Laughlin Pittsburgh Works, designated as P1, P2, P3S, P3N, and P4. The Jones and Laughlin plant was selected for testing of battery stack emissions because the plant uses the silica dusting maintenance technique, coupled with spray patching and troweling. This technique was used on several of the batteries, including P4, which was selected for testing because it provided the best testing location: in the underground rectangular duct that carries the flue gases from the waste heat canal to the battery stack.

Battery P4 is a 79-oven Koppers underjet battery, underfired with undesulfurized coke oven gas. A gas desulfurization unit is nearing completion but was not in operation during the testing. The P4 battery was originally started up in 1953. It underwent a hot end-flue rehabilitation in 1976 and was placed back in operation in early 1977. The battery was operating on a 17-hr coking time during the testing. Other information about the battery is shown in Table 3.1.

Use of silica dusting on battery P4 was begun in early 1978 and has continued since then. Each oven has been "dusted" at least once and some as much as four times. The dates when each oven was dusted are shown in Table 3.2 along with the pressure rise in the oven, in inches of

TABLE 3.1 PLANT DESIGN AND OPERATION RECORD

Date Monday, April 30, 1979

Plant Name Jones and Laughlin

Plant Location Pittsburgh, Pennsylvania

Battery No. P-4

Name of Plant Contact Mr. Jim Saunders, Assistant Superintendent, By-Products Department

Type of Ovens and Designer Koppers - Underjet

Date Built Started up in 1953

Date of Last Rehabilitation Early 1977

Type of Last Rehabilitation Hot end flue rehabilitation

Number of Ovens Total 79 In Service 79, except 1 for dusting

Size of Ovens Height 13 ft, Width 17 in., Length 40 ft

Type of coke produced Metallurgical

Normal coking time (hr) 17

Coal charged per oven (tons) 16 to 16.5 Produce about 11.0 tons of coke

Reversal period (min) 30 min

Nozzle decarbonization method Part of flue gas is recirculated to decarbonize

Is flue gas recirculated? (See above)

Type of fuel gas COG Heating value _____ Btu/scf

Is fuel gas desulfurized? No.

Note use of stage charging, preheated coal, etc. Stage charging

Stack height and top diameter 225 ft 12.5 ft ID at bottom, 9.5 ft ID at top

Test location (stack or waste heat canal) 8 by 8 ft (provide sketch)

Control method used Patching and silica dusting

Fuel gas analysis		Coal analysis	
Component	Vol.%	Component	Vol.%
CO_2		Ash	
Ill.		S	
O_2		H_2O	
CO		VM	
H_2			
CH_4			
N_2			
H_2S			

JL-42768

TABLE 3.2. RECORD OF DUSTING AND PRESSURE RISE IN OVEN DURING DUSTING (IN. H_2O)

1	2	3	
6/15/78-7.8	3/19/78-5.0	3/3/78-4.2 8/11/78-7.6	1
6/19/78-8.4 9/9/78-7.7	5/16/78-4.2 11/5/78-6.0	2/10/78-2.9 11/16/78-6.0	2
5/17/78-6.1 8/9/78-8.0	5/11/78-4.9 8/31/78-4.0	5/26/78-4.0	3
3/12/78-7.9 8/24/78-8.6	3/6/78-4.9 7/30/78-6.4	5/22/78-5.0 4/1/79-5.1 7/1/78-7.2	4
6/1/78-5.0 7/12/78-8.0	4/14/78-6.1	4/19/78-6.4 8/14/78-6.0	5
5/7/78-7.4 11/26/78-4.0	3/22/78-5.4 12/2/78-6.4 7/6/78-5.8	4/26/78-3.0 7/13/78-6.0	6
6/10/78-5.0 7/26/78-7.4	4/26/78-5.5 11/14/78-6.0	5/15/78-5.0	7
5/25/78-5.0 8/16/78-6.0	5/5/78-6.0 8/6/78-6.4	6/22/78-7.6	8
6/6/78-4.5 10/20/78-7.8 7/3/78-6.0	5/21/78-6.1 3/27/79-2.8 8/1/78-7.6	6/13/78-6.6	9
6/25/78-4.0	5/10/78-4.2 6/30/78-6.0	6/17/78-8.1 8/29/78-8.4	10
6/23/78-7.3 7/18/78-7.4	8/25/78-4.3 8/19/78-7.4 7/4/78-5.0	6/27/78-6.8	11
3/14/78-4.1 7/25/78-8.4	4/18/78-6.0 11/24/78-7.4 9/22/78-3.0 4/4/79-2.8	5/14/78-5.2	12
6/27/78 11/11/78-6.5 10/30/78-8.8	4/5/78-6.3 7/16/78-6.2	6/18/78-5.1	13
6/20/78-3.1 9/20/78-7.4	5/20/78-6.1 11/13/78-7.2	6/24/78-7.6 1/2/79-4.5	14
6/26/78-4.2 7/20/78-5.0	5/4/78-7.5	6/11/78-8.4	15
6/12/78-6.3	5/26/78-6.5 11/3/78-7.6	6/25/78-7.2 11/7/78-7.0 10/14/78-8.0	16
6/14/78-8.5	5/13/78-5.0 7/5/78-5.4	6/22/78-7.2 10/18/78-7.0	17
6/3/78-4.2	5/18/78-6.2	6/8/78-4.0	18
4/2/78-5.4 7/21/78-6.5 7/11/78-5.5	6/4/78-5.0 10/28/78-6.8	4/8/78-5.9 4/3/79-3.8 7/24/78-9.0	19
3/3/78-3.9 7/23/78-8.2	4/28/78-7.4 3/28/79-4.0 7/14/78-8.7	3/2/78-5.7 10/2/78-7.0	20
2/7/78-1.0 11/12/78-7.2	6/8/78-4.3 7/9/78-6.0	3/16/78-3.7 11/22/78-4.0	21
3/30/78-5.3 7/10/78-7.2	4/21/78-8.0 11/8/78-9.7 9/13/78-5.0	3/24/78-4.1	22
4/15/78-5.0 5/23/78-6.2	6/6/78-3.9 11/18/78-5.0	3/8/78-4.3	23
4/28/78-4.0 10/8/78-7.0 7/7/78-7.8 11/1/78-7.2	5/1/78-7.0	4/4/78-6.0	24
3/1/78-4.2	5/31/78-5.0 9/6/78-7.0	5/2/78-5.0	25
5/8/78-3.9 10/27/78-7.4	6/12/78-5.0 4/30/79-4.0 8/3/78-7.2		26
7/26/78-5.0 8/27/78-7.8	3/19/78-5.0		27

water, that is measured during the dusting. This table shows only the dates when patching and dusting occurred, but not the dates when additional patching without dusting may have been carried out.

During 1978, the ovens were patched and dusted more frequently than in 1979, but on a random basis. Recently Jones and Laughlin has instituted a systematic maintenance technique utilizing computerized maintenance record keeping that includes observation of whether the stack "smoked" or did not "smoke" after charging of specific ovens. The computerized records show the type and date of any oven maintenance and the date the stack was observed and the number of minutes that the stack smoked after a specific oven was charged. These data are now used to select ovens which should be dusted, rather than the random basis on which ovens were previously selected for dusting. Jones and Laughlin personnel believe this computerized information system should enable them to achieve much better control of battery stack emissions.

The actual patching and dusting operation usually requires at least 24 hours in which an oven is out of service. During the first 8 hours, spray patching and troweling of the end flues is carried out by a three-man crew, on both the coke side and pusher side of the oven. During the next shift, a three-man crew "dusts"

the oven with all doors and lids closed and sealed. This takes 2 to 3 hours and uses about 100 lb of the silica dust. The dust is hand-fed into a small hopper that is air aspirated to disperse the dust and carry it into the oven through a special charging lid. Pressure rise in the oven is monitored during this operation and usually increases from 3 to 8 in. of water.

No "dusting" was carried out during the testing because of possible interference with the particulate tests. However, a dusting operation on one oven was observed on the day preceding the first test, It was observed that silica dust leaked out the chuck door at first. The chuck door was tightened, after which the dust began leaking out the coke-side door. We were told that this was an abnormal example of the dusting operation but it does demonstrate some of the problems that can occur when using this technique. Overall, the condition of the walls in the P4 ovens appeared to be very good, with few visible cracks in any of the ovens.

During each test day process operating data was obtained at approximately 1-hr intervals, and the time that each oven was pushed and leveled was recorded whenever possible. Copies of circular charts showing process data were obtained, along with coke and coal analyses done by Jones and Laughlin, and fuel gas analysis. Also,

some flue inspections were made and noted along with other observations or information. All of these records are shown in Appendix I.

Jones and Laughlin personnel cooperated with the test team during the testing, and appreciation is expressed for the help provided by Mr. Jim Saunders, Assistant Superintendent, and Mr. Ken Kobus, Heater Foreman.

4.0 LOCATION OF SAMPLING POINTS

The underground waste heat duct sampling location was accessed through a vertical cut-off damper slot, located approximately 42-feet downstream from the battery waste heat flue centerline and 60-feet upstream of the battery stack. The duct itself is located 4 - feet 3 - inches below ground level with an 8 x 8-foot (nominal) cross-section. This particular location was selected since there was no feasible method to install ports in the concrete battery stack. The damper slot measured approximately three inches across at the ground level elevation and tapered to one-inch across at the underground duct entry point.

The six sampling ports on top of the damper slot were spaced 16 inches on center. Each vertical traverse consisted of five sampling points; six were originally proposed but, due to an irregular build-up of deposit on the bottom of the duct, the sixth point was eliminated. Velocity pressures and temperatures were measured at each of the 30 sampling points. Figure 4.1 is a diagram of the sampling location showing each of the traverse points and their respective distances from the duct walls.

Points	Vertical Distance Inside Duct	
	feet	centimeters
1	0.7	21.3
2	2.1	64.0
3	3.5	106.7
4	4.9	149.4
5	6.3	192.0

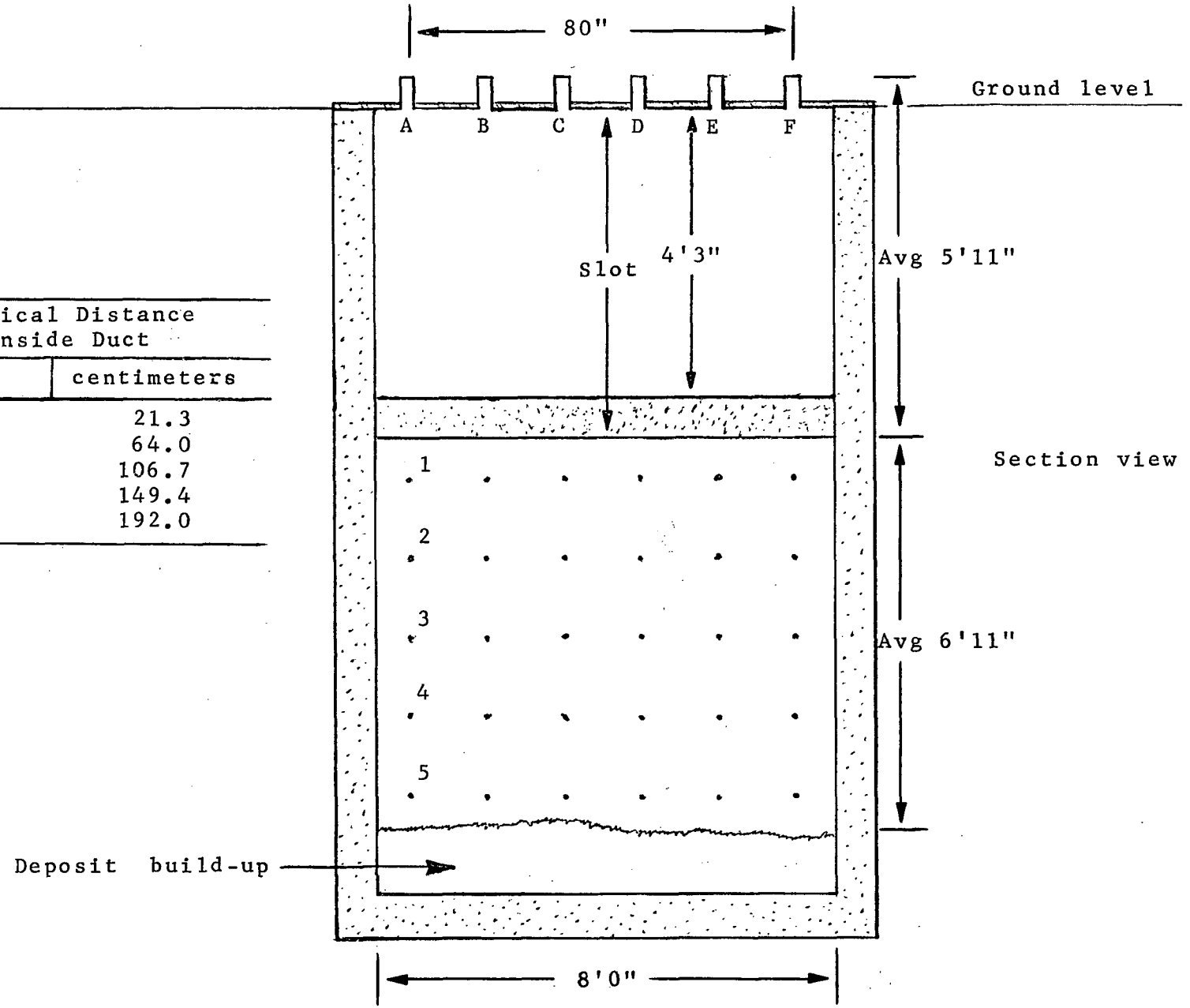


Figure 4.1. Sampling location - waste heat duct.

5.0 SAMPLING AND ANALYTICAL PROCEDURES

PARTICULATE EMISSIONS

Triplicate two and one-half hour particulate samples were extracted isokinetically for five minutes at each of 30 sampling points in the waste heat duct. During each test, the probe, Pitot tube, and thermocouple assembly were moved to each sampling point, the velocity pressure and temperature of the exhaust gas were measured, and isokinetic sampling flowrates were adjusted accordingly. An orifice-type meter was used to indicate instantaneous flowrates.

Proper nozzle alignment with the flue gas stream was maintained throughout the test by clamping the probe assembly at the top of each port. As a result of this vertical support system, there was no unusual difficulty in measuring the actual gas velocity pressures. The impinger assembly was moved as required to gain access to each vertical entry port. Some interference was anticipated from the push ram (on the pusher car) passing above the sampling location; however, proper synchronization of the push ram operation with the probe position eliminated this potential problem. All field data sheets are included in Appendix B.

The sampling train was checked for leaks before and after each sample run in accordance with the requirement that the initial leak rate shall not exceed 0.02 ft^3/min at 15 inches of mercury vacuum and the final leak rate shall not exceed 0.02 ft^3/min at the greatest vacuum incurred during the test.

A modified EPA Method 5 sampling train was used (Figure 5.1). The sampling train consisted of a sharp, tapered, stainless steel sampling nozzle; a 14-foot stainless steel probe assembly (instead of glass); a heated preweighed 110-mm glass-fiber filter; flexible Teflon® tubing leading to two Greenburg-Smith impingers, the first modified, the second standard, each containing 100-ml of distilled water; an empty modified Greenburg-Smith impinger; a modified Greenburg-Smith impinger containing approximately 400 grams of silica gel; a leakless pump with vacuum gauge; a calibrated dry gas meter equipped with bimetallic inlet and outlet thermometers; and, a calibrated orifice-type flowmeter that was connected to a 0-to-10-inch range inclined (water gauge) manometer. As a result of the unusual configuration of the underground sampling location, it was impossible to utilize a 14-foot glass probe for sample extraction, due to obvious difficulties with flexing and fracturing.

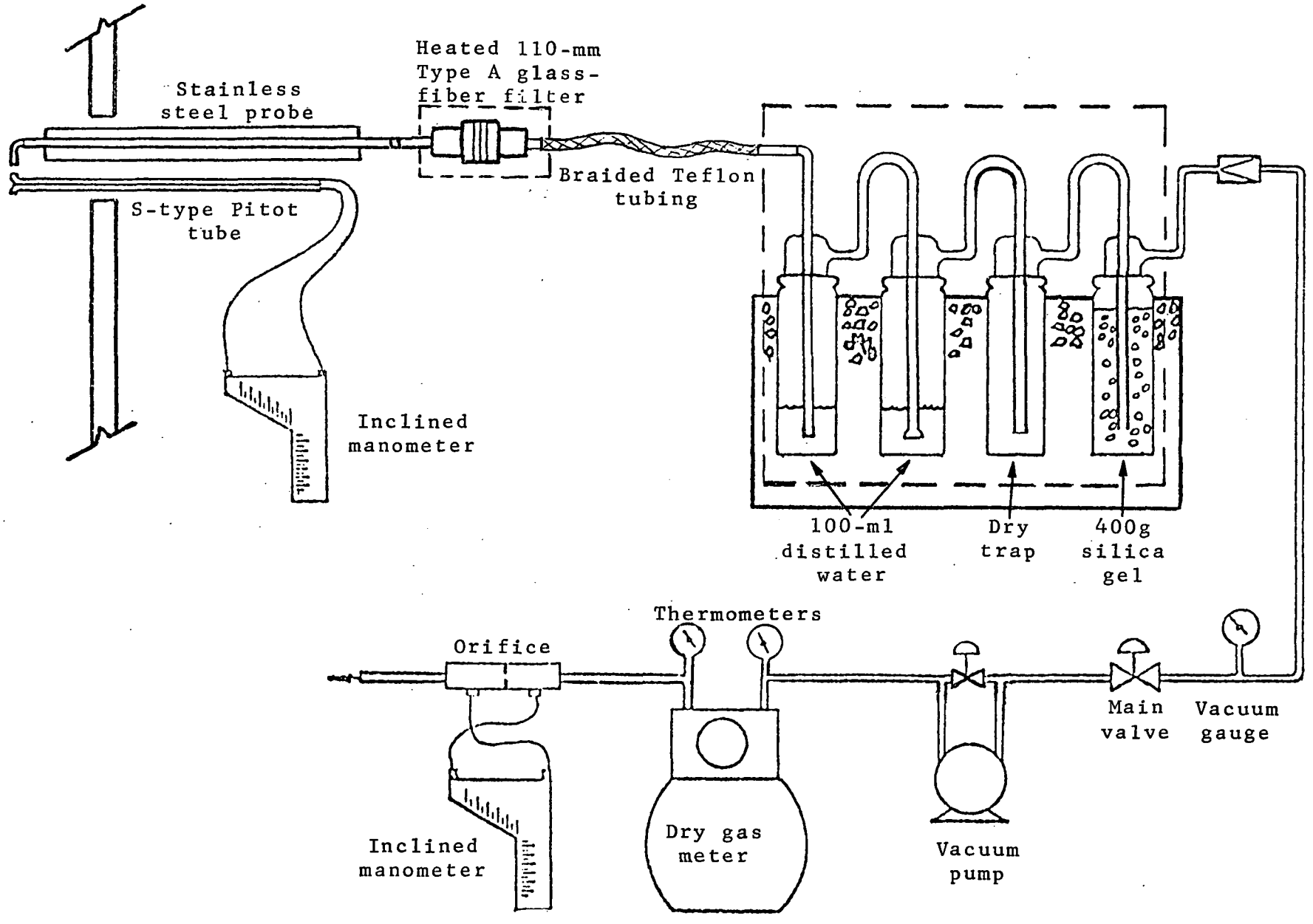


Figure 5.1. Particulate sampling train.

The impinger train was immersed in an ice bath to maintain the temperature in the last impinger at 70F or less. All of the sampling train glassware was connected by ground glass joints, sealed with stopcock grease, and clamped to prevent leakage. A calibrated S-type Pitot tube was connected to the sampling probe and velocity pressures were read on the inclined manometer. An iron-constantan (I/C) thermocouple, attached to the Pitot-probe assembly, was connected to a calibrated pyrometer. During the course of testing, the filter temperature was kept at 250 $\pm$ 25F.

Following each sample run, the entire sampling train was transferred to a sheltered clean-up area. The probe and nozzle assembly, and the front half of the filter holder were initially rinsed and brushed with water, then acetone. The two rinsings were collected in separate glass sample bottles with Teflon® -lined caps. The glass-fiber filter was returned to its original petri dish and sealed. The volumes of the impinger contents were measured and volume increases recorded. The solutions were placed in glass sample bottles with Teflon®-lined caps. The impingers were first rinsed with water, then acetone. The water rinsings were placed in the same sample bottle as the impinger solutions,

and the acetone rinsings were placed in a separate glass sample bottle. The flexline and back-half of the glass filter holder were brushed and rinsed with water, then acetone, and the rinsings placed in the respective sample bottles. The silica gel was weighed to determine the weight gain (as condensate).

Thus, five fractions were collected for each particulate sample:

(1) water rinsings of probe and nozzle assembly, and front-half of the filter holder;

(2) acetone rinsings of probe and nozzle assembly, and front-half of the filter holder;

(3) 110-mm type A glass-fiber filter;

(4) impinger contents and water rinsings of back-half of filter holder, flexline, and impingers; and

(5) acetone rinsings of back-half of filter holder, flexline, and impingers.

Filterable particulate was the sum of Fractions 1, 2, and 3. Total particulate was the sum of Fractions 1 through 5. The particulate weights by fraction are presented in Appendix C.

In the laboratory, the liquid fractions were measured volumetrically and placed in tared beakers. A five milliliter aliquot was taken from each fraction for sulfate analysis. The water fractions were then evaporated to residue at 105C and the particulate weight determined. The acetone fractions were evaporated at room temperature and weighed until constant. The filter was desiccated at room temperature and weighed until constant. All weight determinations were performed on an analytical balance having a sensitivity of 0.1 milligrams.

For the determination of sulfates in the liquid samples, the 5-ml aliquot was brought up to 25-mls with 80-percent IPA. The filter was also combined with 80-percent IPA. The acidity was adjusted with perchloric acid to a pH of between 2.5 and 4.0. Three to five drops of thorin indicator were then added and the solution titrated with standardized barium perchlorate. The results are reported as sulfuric acid (including sulfur trioxide), and as a percent of total particulate.

CARBON MONOXIDE SAMPLING

A sample of flue gas was drawn through a stainless steel probe, Teflon® tubing, and then through a particulate and condensate trap containing a glass wool plug, to a 3-way valve. This valve was used to

divide the gas sample into two streams; one for the continuous analysis of carbon monoxide and one to provide an integrated bag sample for the determinations of benzene content and exhaust gas composition by the Orsat method.

The gas stream used for carbon monoxide monitoring was then passed through two modified Greenburg-Smith impingers, the first containing approximately 250 grams of silica gel and the second containing approximately 500 grams of Ascarite®, for moisture and carbon dioxide removal, respectively. Finally, a leak-free diaphragm pump forced the sample through a needle valve to a rotameter and the Beckman Model 865 NDIR analyzer. At the sample interface, a flowrate of approximately 1.5 cfh with a delivery pressure of 10 psig was maintained for the duration of the continuous sampling. An analog strip chart recorder was used to record all instrument outputs. This sampling system is depicted in Figure 5.2.

The daily calibration sequence included passing a certified standard zero gas (dry nitrogen) and a certified standard span gas in concentrations of 9,900 ppm or 29,800 ppm carbon monoxide in nitrogen through the analyzer. The instrument output was calibrated for two anticipated ranges, 0-10,000 and 0-30,000 ppm carbon monoxide by adjustment of the

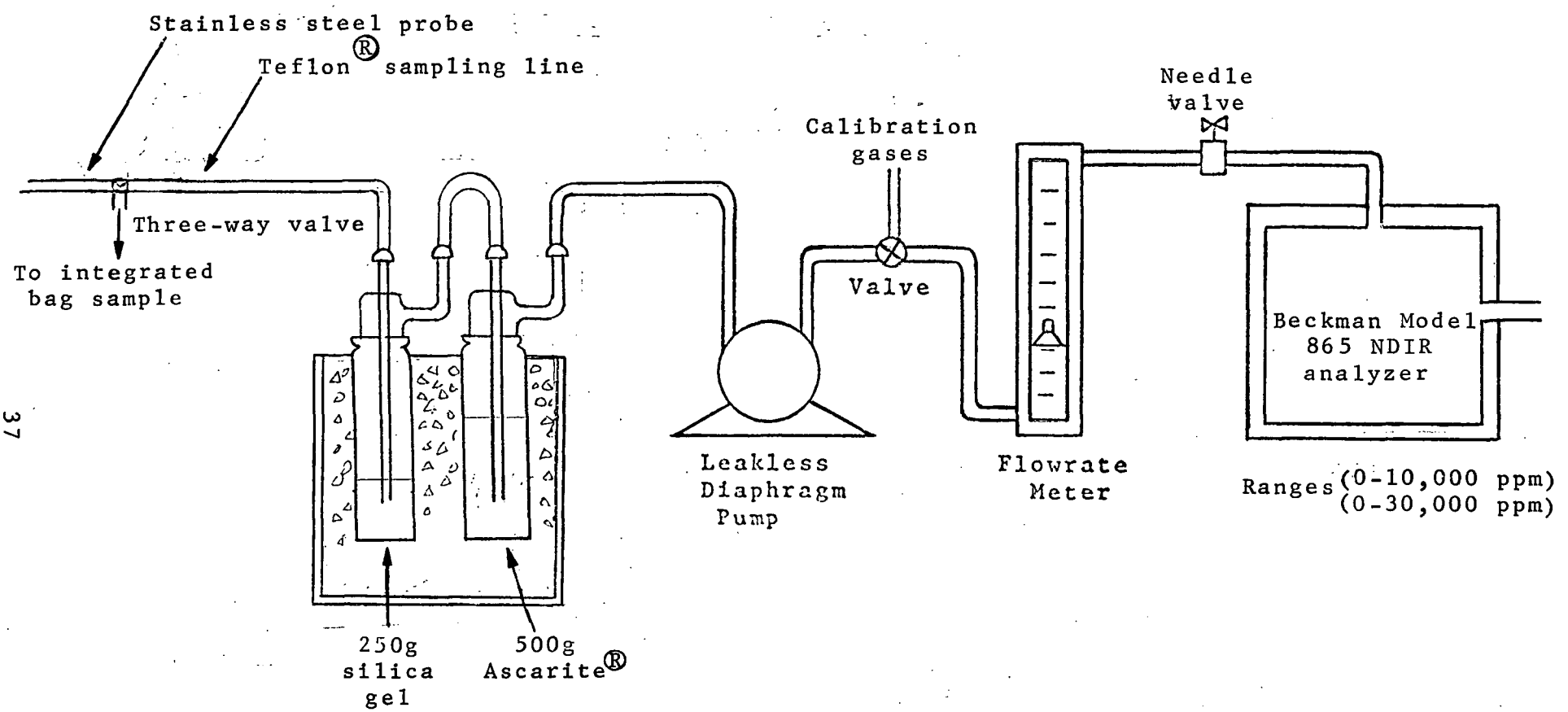


Figure 5.2. Sampling train for continuous monitoring of carbon monoxide.

zero and gain settings for the appropriate signal, as indicated on a calibration curve. The instrument operates by the Luft principle as specified in Reference Method 10. A 4-position valve allows the introduction of sample gas or any of the required standard calibration gases.

The actual measured concentrations of CO were determined by adjusting the recorded strip chart values with the factory calibration curve for the 16-mm cell, which had been adjusted to the standard gas concentrations used in the field.

INTEGRATED BAG SAMPLING (BENZENE AND ORSAT)

An integrated bag sample was withdrawn from the waste heat duct simultaneously with each particulate sampling run utilizing a train as depicted in Figure 5.3, and as described previously under Carbon Monoxide Sampling. An evacuated Tedlar® bag with a volume of 100 liters was placed inside an insulated steel drum. The drum was then gradually evacuated, thereby filling the Tedlar® bag at a controlled flowrate, using a rotameter and valve assembly as shown in Figure 5.3. When the bag was filled, it was removed and transferred to a laboratory for immediate gas chromatographic (GC) analysis of the benzene content and later, Orsat analysis.

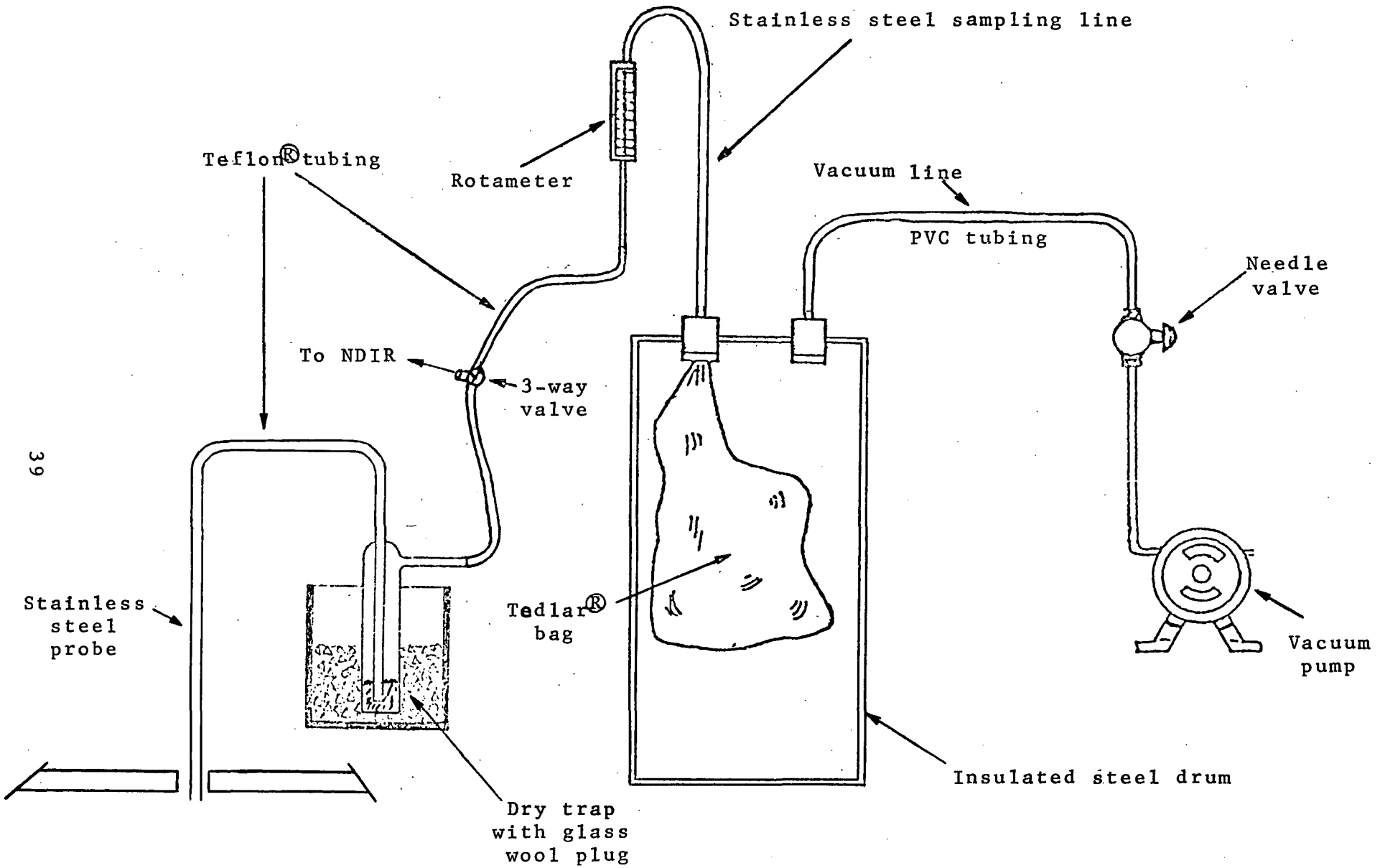


Figure 5.3. Integrated bag sampling train.

The method used for the determination of benzene concentrations is in accordance with the EPA gas chromatographic Method 110, "Determination of Benzene from Stationary Sources", delineated in Appendix F-1. Gas chromatographic field analyses were performed utilizing an Analytical Instrument Development (AID) Model 511, portable gas chromatograph with a flame ionization detector and a 6' x 1/8" stainless steel column packed with 1.75-percent Bentone and 5-percent SP1200 on 100/120 mesh Supelcoport. The following operating conditions were maintained for all analyses: 85C oven, 105C detector, 190F gas sampling loop with 1 ml capacity, and 16 ml/min zero nitrogen carrier gas. The samples were analyzed for benzene on the same day they were collected. Peak areas were measured using a compensating polar planimeter. The sample chromatograms had three apparent peaks, which were completely resolved.

Following the GC analyses, each integrated bag sample was analyzed by the Orsat method for carbon dioxide, oxygen, and carbon monoxide concentrations, as specified in EPA-Method 3. These results were used to calculate the molecular weight of the process gas.

Visible Emissions

Visible emissions from the P4 battery stack exhaust were recorded for the duration of each sample run except for Sample No. 3, for which visible emissions were abbreviated due to foul weather. The observations were performed in accordance with EPA Method 9 by a qualified visible emissions observer. A summary of the visible emission data is presented in Appendix B-4.

SECTION II - TRW REPORT

Log of B(a)P tests the Product Coke Oven Battery Stack, Jones and Laughlin Steel Corporation, Pittsburgh, Pennsylvania plant.

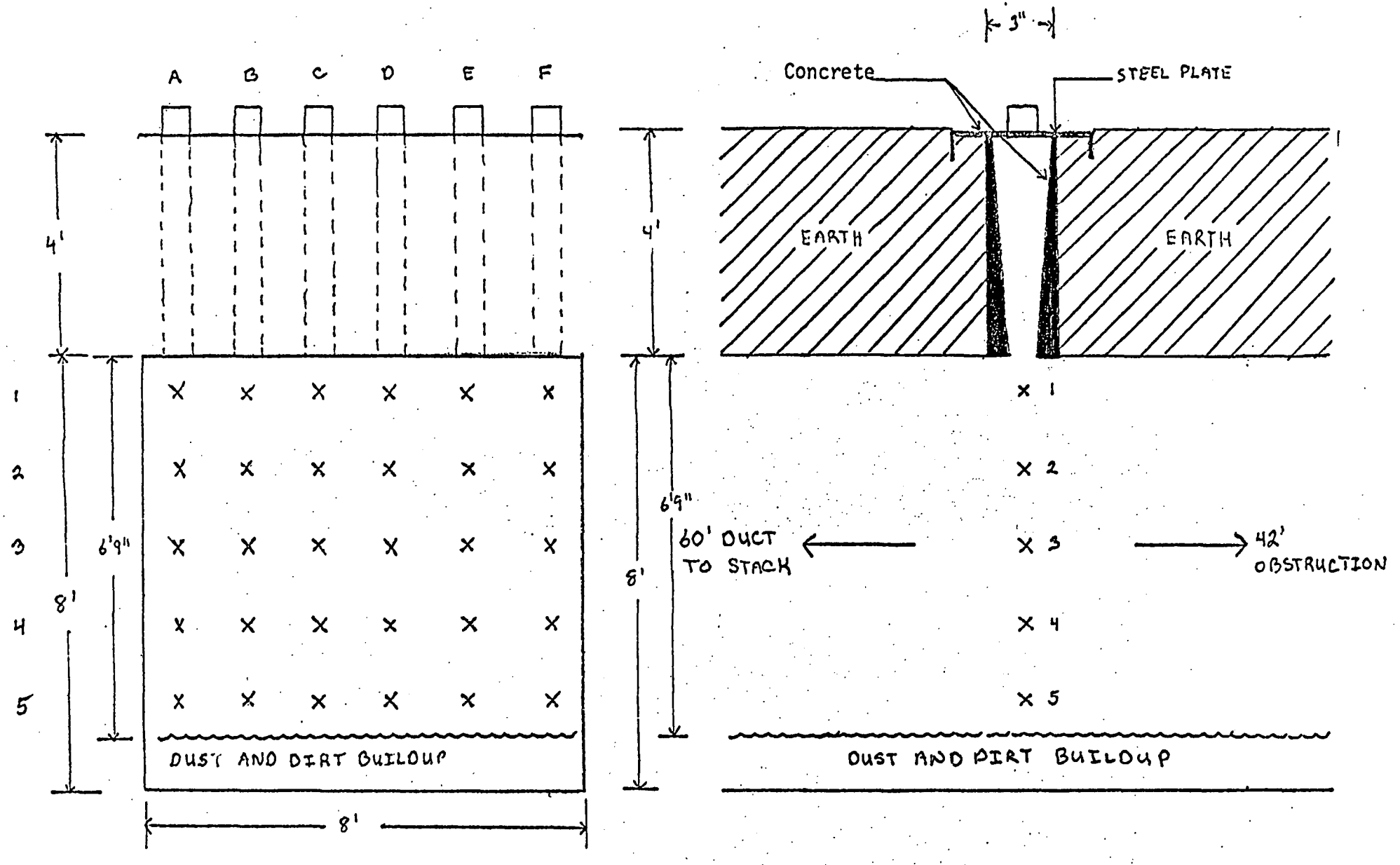
Monday, April 30, 1979

TRW spent the day preparing for the first B(a)P test which was to be run simultaneously with the Clayton Environmental Consultant's particulate test. It was considered that TRW would follow Clayton and use Clayton's pitot values for TRW's run since TRW did not have their own pitot of sufficient length.

EPA's Technical Manager, Mr. Frank Clay requested TRW to try and rig a temporary pitot for the three B(a)P runs. The pitot was constructed with a 10-foot stainless pitot and a 6-foot of Teflon tube which was connected to the metal tube by rubber hose and taped. Clayton checked the duct and found a dust and dirt build-up at the bottom which naturally changed the effective duct size (Figure 1).

TRW cleaned the sampling train after which blanks were taken from each of the train's components, the same as after a normal sampling run. After this, all major components were leak checked and capped ready for the first test. See Figure 2 for sampling train configuration.

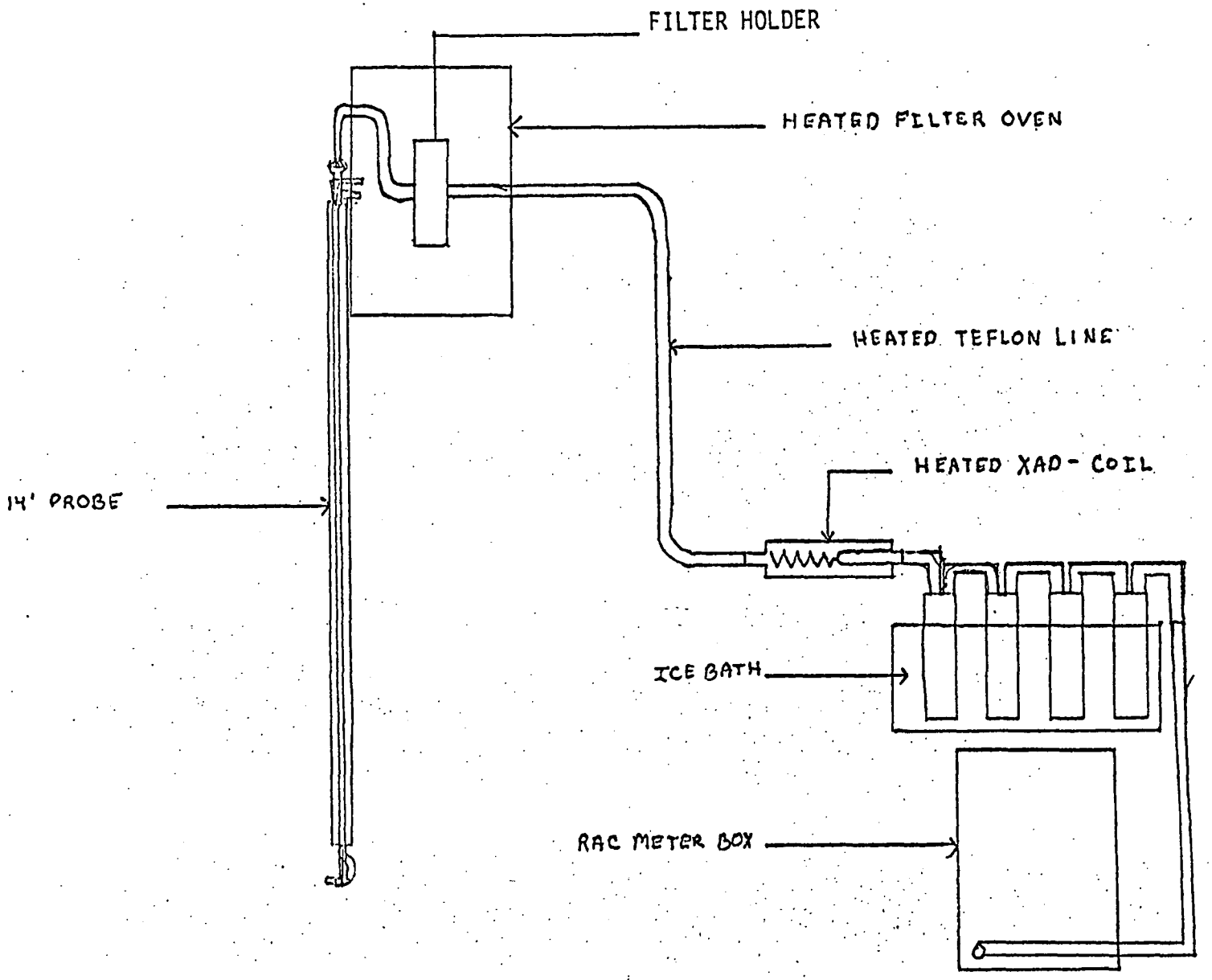
FIGURE 1



FRONT VIEW WITH OBSERVERS BACK TO THE EXHAUST STACK

SIDE VIEW

FIGURE 2


FILTER HOLDER
HEATED FILTER OVEN
HEATED TEFLON LINE
HEATED XAD - COIL
14' PROBE
ICE BATH
RAC METER BOX

Tuesday, May 1, 1979

TRW arrived at site and set up the train for the first test. During the leak check the heated Teflon hose collapsed. The heated hose was replaced and sampling started at 1450. At 1555 it was discovered that the female inlet to the XAD-2 coil was cracked. It was leak checked to be airtight but it was expected that it would start leaking later so it was replaced. While the coil was being replaced it is thought that the taped tubing of the pitot developed a leak which affected pitot reading on the last three points of the remaining ports and the same points on the first three ports of the second test.

No problems were encountered except for trying to keep the gas temperature at the exit of the XAD-coil at 127F. The temperature tended to fluctuate, and at times, it was impossible to reach 127F. The final leak check was .02 at 15" of mercury. The test was completed at 1842.

While recovering the sample it was noticed that the water in the first impinger was discolored, a mixed tan and brown color.

Wednesday, May 2, 1979

Second test started at 1043 with no problems, and finished at 1356. The impinger water was not discolored at the end of the test.

Thursday, May 3, 1979

Testing started at 1049 and finished 1442. No major problems were encountered. It was still impossible to hold the XAD-2 coil's exit gas to 127F but it was possible to hold in a ±20F range of 120-127F.

Discussion of Tests

For results of the tests see Table 1 and 2. Since TRW's pitot readings were somewhat questionable it was decided to use both TRW's and Clayton's pitot results to calculate the duct flow rates.

Due to the electric shock hazard caused by the high temperatures of the duct burning off the probes insulation it was decided not to heat the probe. The filter oven temperature was monitored by taping a thermocouple to the inlet of the filter. The flex line was heated using heat tapes controlled by a Variac, and the XAD-2 coil was heated using a water bath system. The temperature was monitored by taping a thermocouple to the outlet of the XAD-2 coil. It was possible to maintain the filter temperature at 248F± 25 F during most of the testing period. The XAD-2 coil was controlled at 122F± 18 F during most of the testing period.

TABLE 1

BαP - TEST RESULTS

TEST #	BαP-JL-1	BαP-JL-2	BαP-JL-3	3 RUN AVERAGE
DATE	5/1/79	5/2/79	5/3/79	
TRW DATA				
METER VOLUME DSCF	88.025	74.032	98.539	86.8695
METER VOLUME DSCM	2.493	2.097	2.791	2.460
DUCT VOLUME ACFM	94,856	79,337	113,243	95,812
DUCT VOLUME DSCFM	40,548	33,498	47,282	40,442
DUCT VOLUME DSCMM	1148.3	948.7	1339.0	1145.3
% ISOCKINETIC	105	108	104	
CLAYTON'S DATA				
DUCT FLOW ACFM	112,607	96,020	115,503	108,043
DUCT FLOW DSCFM	47,626	40,088	48,176	45,297
DUCT FLOW DSCMM	1348.8	1135.3	1364.4	1,282.8
% ISOKINETIC USING TRW METER VOLUME AND CLAYTON DUCT FLOW	89	91	102	

TABLE 2

J & L - BαP TEST RESULTS

SAMPLE	μg/FILTER	μg/PROBE RINSE	μg/HEATED HOSE	μg/XAD-2	μg/TOTAL	DUCT FLOW *DSCMM	METER VOLUME DSCM	μg/DSCM	gm/HR	DUCT FLOW DSCFM	METER VOLUME DSCF
BαP-JL-1	< 0.002	1.6170	0.4674	<0.001	2.0874	1345.8	2.493	8.35×10^{-4}	0.0672	47,626	88.025
BαP-JL-2	<0.002	0.4329	0.3150	<0.001	0.7509	1135.3	2.097	3.58×10^{-4}	0.0241	40,088	74.032
BαP-JL-3	0.050	0.1710	0.3780	<0.001	0.6100	1364.4	2.791	2.18×10^{-4}	0.0177	48,176	98.539
3 RUN AVERAGE	< 0.021	0.7403	0.3868	<0.001	1.1494	1282.8	2.462	2.70×10^{-4}	0.0363	45,296	86.940

SAMPLE	LBS/DSCF	LBS/HR	LBS/24 HR DAY	LBS/365 DAYS	*** YEARS/LB
BαP-JL-1	5.21×10^{-11}	1.48×10^{-4}	3.55×10^{-3}	1.29	0.78
BαP-JL-2	2.23×10^{-11}	0.53×10^{-4}	1.27×10^{-3}	0.46	2.18
BαP-JL-3	1.36×10^{-11}	0.39×10^{-4}	0.94×10^{-3}	0.34	2.94
3 RUN AVERAGE	2.93×10^{-11}	0.80×10^{-4}	1.92×10^{-3}	0.70	1.43**

* Based on Clayton Environmental Consultants' pitot and temperature readings

** lbs/365 days must be used to derive years/lb.

*** Years required to emit one pound

Due to the minute quantities of B(a)P present in the stack gas relative to the total volume of stack gas, it is difficult to conceive the concentrations in perspective. If the average weight in pounds of B(a)P emitted per dry standard cubic foot (dscf) of stack gas is used with the average dscf per minute stack gas volume, then it is possible to calculate the number of days of continuous operation needed to emit one pound of B(a)P. Based on the data in this report, the time required to emit one pound of B(a)P from the battery stack is 526 days, or 1.44 years (1 year, 5 months, 8 days approximately).