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Iron and Steel (Coke Oven Battery Stack)

Emission Test Report C F & I Steel Corporation Pueblo, Colorado

Emission Testing at a By-Product Coke Plant (Battery D Stack)

C.F. & I. Steel Corporation
Pueblo, Colorado

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

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EMB REPORT NO. 79-CKO-16

Work Assignment 16

Contract No. 68-02-2817

FOREWARD

Two firms prepared this report under contract to the U.S. Environmental Protection Agency; therefore, it is presented in two sections.

Section I was prepared by Clayton Environmental Consultants, Inc., Southfield, Michigan, and includes test results for particulate, sulfate, and chloroform/ether extractables; NO_x (Method 7); continuous monitoring of CO, O_2, and NO_x; O_2, CO, CO_2 (Method 3); and, visible emission data for the Battery D stack exhaust.

Section II was prepared by TRW Energy Systems Group, Redondo Beach, California, and contains the benzo(a)pyrene (B(a)P) sampling data and summary, which immediately follows Appendix H of Section I.

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1.0 INTRODUCTION

The U.S. Environmental Protection Agency retained Clayton Environmental Consultants, Inc., to determine particulate and various gaseous emissions from the battery stack of Coke Oven Battery D at C.F. & I. Steel Corporation in Pueblo, Colorado. 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-16, Contract No. 68-02-2817, Work Assignment 16.

The testing program included the following:

(1) Triplicate samples to be analyzed for particulate, sulfate and chloroform/ether extractables (of the impinger solution);

(2) Integrated bag samples for Orsat analyses;

(3) Continuous monitoring of carbon monoxide, nitrogen oxides and oxygen during the particulate runs;

(4) Grab samples for nitrogen oxides;

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

Auxiliary data included exhaust gas temperatures and flowrates, as determined from the traverses.

The study was conducted on August 7, 8, and 9, 1979 by Clayton Environmental Consultants, Inc. with the continuous nitrogen oxides and oxygen monitoring efforts subcontracted to York Research Corporation of Denver, Colorado. Project participants are listed in Appendix A.

2.0 SUMMARY AND DISCUSSION OF RESULTS

Results of the emission study are presented in Tables 2.1 through 2.5. Tables 2.1 and 2.2 present the filterable and total concentrations and emission rates of particulate and sulfate, respectively. The filterable fraction (front half) includes the particulate from the probe, front portion of the filter holder and the filter. Total particulate includes the filterable fraction plus the particulate in the rear half of the filter holder, the impingers, and connecting glassware up to the silica gel impinger. 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 expressed as a percent of particulate by weight. Sulfates are expressed as sulfuric acid (including sulfur trioxide). Nitrogen oxides concentrations and emission rates are presented in Table 2.4. Concentrations are expressed as parts of nitrogen dioxide per million parts of air (ppm) and the corresponding emission rates as lb/hr and kg/hr. Table 2.5 presents the results of the exhaust gas composition (Orsat) analyses.

All field data sheets and continuous monitoring data are included in Appendices B and C, respectively. Appendix D presents an example of calculations used to interpret the data collected.

PARTICULATE RESULTS

The measured filterable concentrations of particulate from Battery D, shown in Table 2.1, ranged from 0.035 to 0.045 gr/dscf (80.4 to 104 mg/dscm) and averaged 0.039 gr/dscf (89.9 mg/dscm). Concentrations of total particulate ranged from 0.043 to 0.064 gr/dscf (98.7 to 147 mg/dscm), and averaged 0.051 gr/dscf (118 mg/dscm).

Emission rates of filterable particulate ranged from 6.76 to 7.21 lb/hr (3.07 to 3.27 kg/hr) and averaged 6.93 lb/hr (3.15 kg/hr). Total particulate emission rates ranged from 8.38 to 9.54 lb/hr (3.80 to 4.33 kg/hr), and averaged 9.02 lb/hr (4.09 kg/hr). Generally, the data reflect good reproducibility (within 10 and 25-percent of the mean, based on concentration).

Run 1 results show a higher concentration of filterable and total particulate than Runs 2 and 3. The emission rates of filterable and total particulate, however, show lower filterable emissions and higher total particulate emissions than Runs 2 and 3. The flowrate during Run 1 was approximately 23-percent lower than during Runs 2 and 3, which contributes to

TABLE 2.1. PARTICULATE CONCENTRATIONS AND EMISSION RATES

Sample Number	Date 1979	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	8-7	17,400	440	0.045	104	0.064	147	6.76	3.07	9.54	4.33
2	8-8	22,600	430	0.037	85.2	0.047	108	7.21	3.27	9.13	4.14
3	8-9	22,700	420	0.035	80.4	0.043	98.7	6.83	3.10	8.38	3.80
Average		20,900	430	0.039	89.9	0.051	118	6.93	3.15	9.02	4.09

the differences in the calculated emission rates between these runs.

SULFATE RESULTS

Table 2.2 presents the measured filterable concentrations of sulfate, which was 0.012 gr/dscf for all three runs (ranging from 26.5 to 28.5 mg/dscm and averaging 27.2 mg/dscm). Concentrations of total sulfate ranged from 0.021 to 0.050 gr/dscf (47.6 to 115 mg/dscm), and averaged 0.032 gr/dscf (72.3 mg/dscm).

Emission rates of filterable sulfate ranged from 1.85 to 2.26 lb/hr (0.841 to 1.03 kg/hr), and averaged 2.12 lb/hr (0.964 kg/hr). Total sulfate emission rates ranged from 4.02 to 7.49 lb/hr (1.83 to 3.40 kg/hr), and averaged 5.37 lb/hr (2.44 kg/hr).

Sulfate, as a percent of the filterable particulate by weight (Table 2.3), ranged from 27.4 to 33.1-percent and averaged 30.5-percent. The total fractions ranged from 44.1 to 78.5-percent and averaged 59.2-percent.

Filterable sulfate concentrations are very reproducible over the three sample runs (0-percent variation about the mean). The emission rates of filterable sulfate are higher in Runs 2 and 3 than in Run 1 despite the similarity in sulfate concentrations, due to the higher flowrates which were measured in these runs. Total sulfate concentrations also

TABLE 2.2. SULFATE CONCENTRATIONS AND EMISSION RATES

Sample Number	Date 1979	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	8-7	17,400	440	0.012	28.5	0.050	115	1.85	0.841	7.49	3.40
2	8-8	22,600	430	0.012	26.5	0.021	47.6	2.24	1.02	4.02	1.83
3	8-9	22,700	420	0.012	26.6	0.024	54.3	2.26	1.03	4.61	2.09
Average		20,900	430	0.012	27.2	0.032	72.3	2.12	0.964	5.37	2.44

TABLE 2.3. SULFATE AS A PERCENT OF PARTICULATE (BY WEIGHT)

Sample Number	Filterable	Total
1	27.4	78.5
2	31.1	44.1
3	33.1	55.1
AVERAGE	30.5	59.2

show reproducibility for Runs 2 and 3 (with a 12-percent variation), but Run 1 shows twice as much total sulfate as Runs 2 and 3. A similar relationship exists in terms of total sulfate emission rates.

Total sulfate, as a percent of total particulate by weight, is 58-percent higher in Run 1 than the average of Runs 2 and 3. This fact, coupled with the higher total particulate concentrations and emission rates encountered in Run 1 versus Runs 2 and 3, and the differences in measured flowrates in these sets of data, suggests a possible difference in the process operating conditions between Run 1 and Runs 2 and 3.

NITROGEN OXIDES RESULTS

Nitrogen oxides concentrations for the Method 7 flask grab samples (Table 2.4) ranged from less than 7.66 to 81.9 ppm, and averaged 43.9 ppm. Emission rates ranged from less than 0.954 to 13.3 lb/hr (less than 0.433 to 6.04 kg/hr), and averaged 7.06 lb/hr (3.21 kg/hr). These averages do not include the "less than" values.

These grab sample results do not closely agree with the continuously monitored measurements of nitrogen oxides which are shown in Figures 2.1, 2.2, and 2.3. These measurements all fall within a range between 80 ppm, which occurred during Run 3 and 130 ppm, which occurred during Run 2. Grab Sample 2 does fall within this range, but Samples 1, 3, and 4 are all much lower

TABLE 2.4. NITROGEN OXIDES CONCENTRATIONS AND EMISSION RATES[a]

Sample Number	Date 1979	Concentrations	Emission Rate	
		ppm	lb/hr	kg/hr
1	8-7	< 7.66	<0.954	<0.433
2	8-8	81.9	13.3	6.04
3	8-8	35.8	5.59	2.54
4	8-9	14.0	2.28	1.04
	Average[b]	43.9	7.06	3.21

[a]Method 7 flask grab samples (as nitrogen dioxide).
[b]Average based on Samples 2, 3, and 4.

Figure 2.1. Graphic display of continuously monitored data.

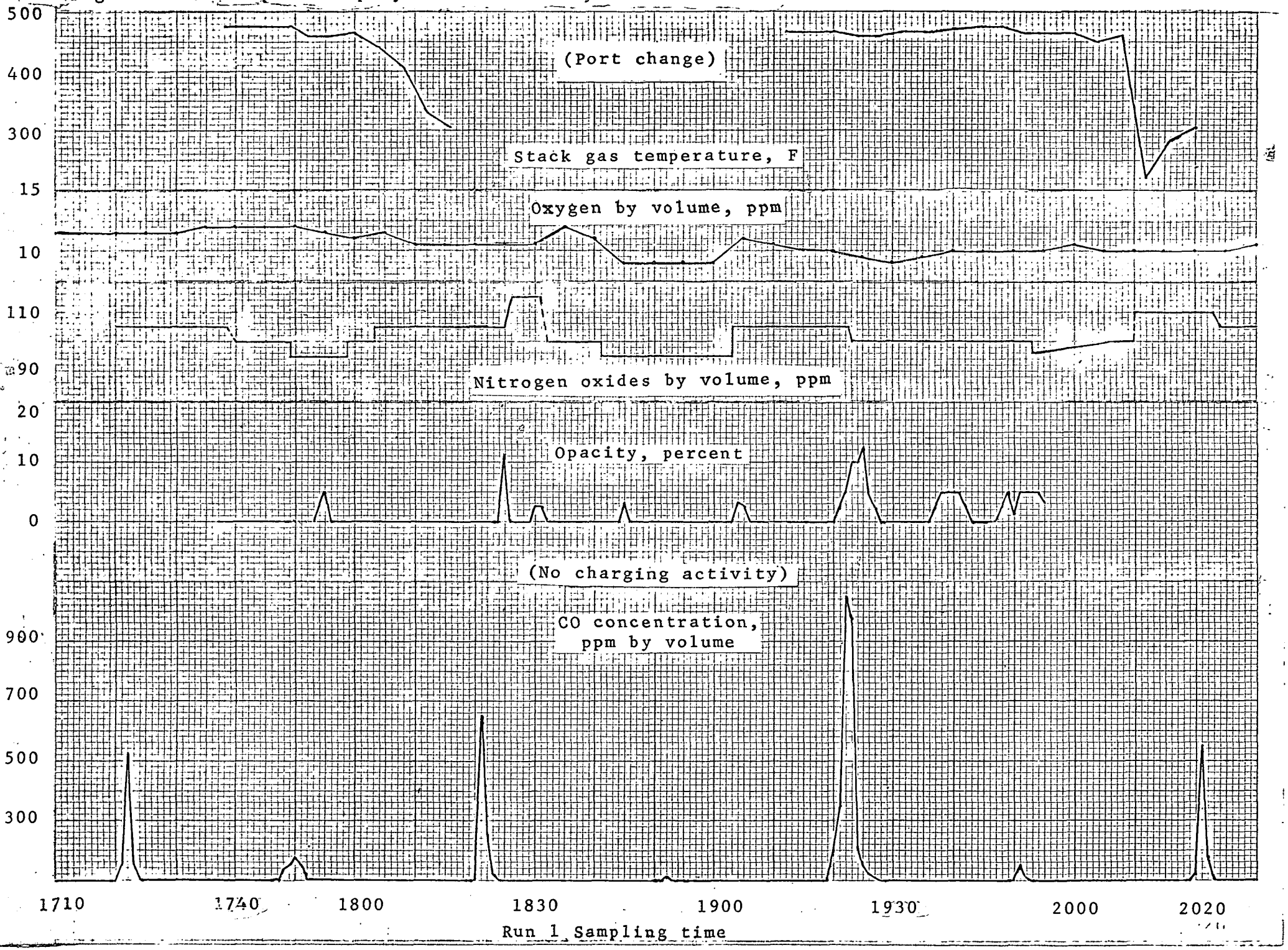


Figure 2.2. Graphic display of continuously monitored data.

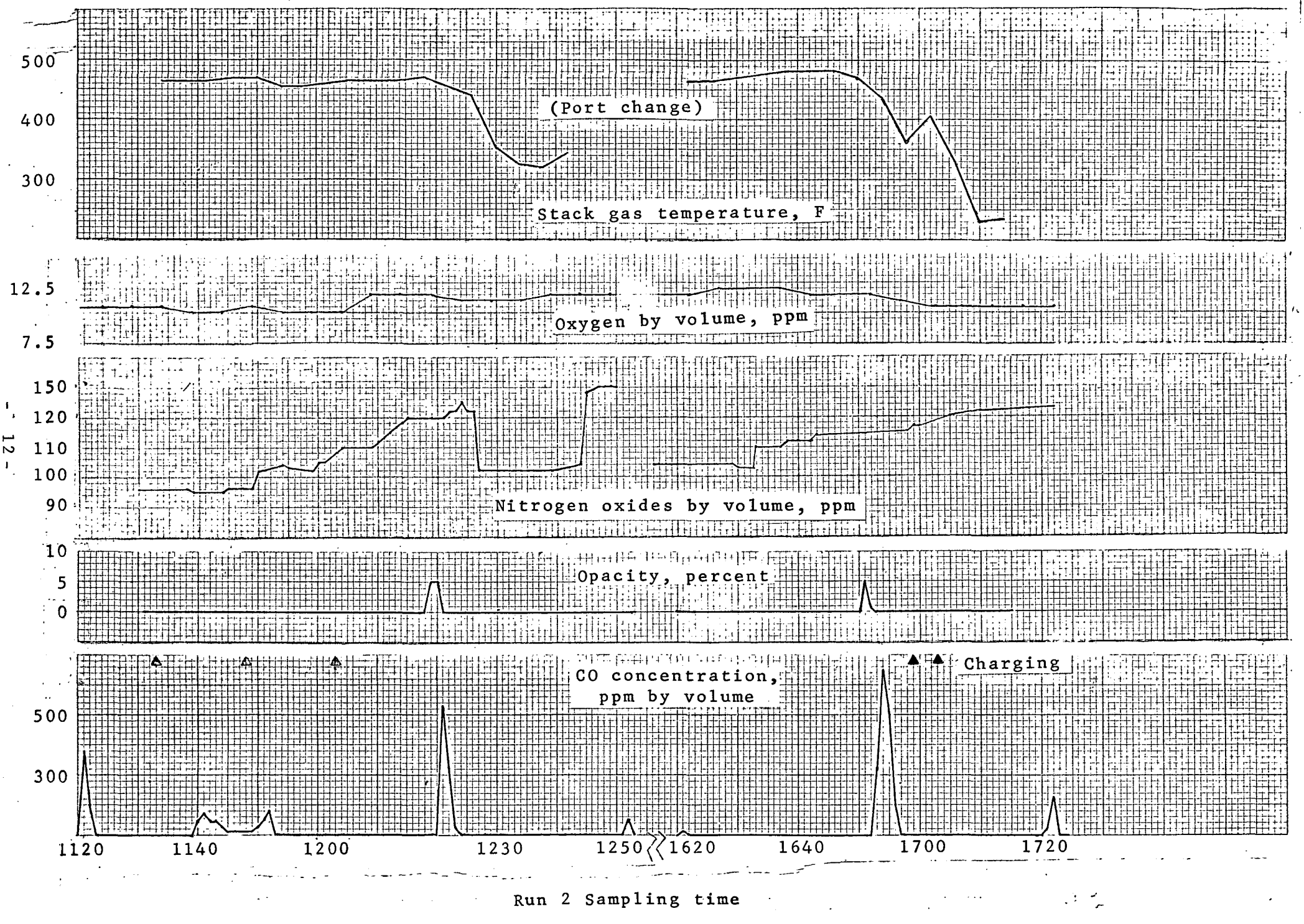
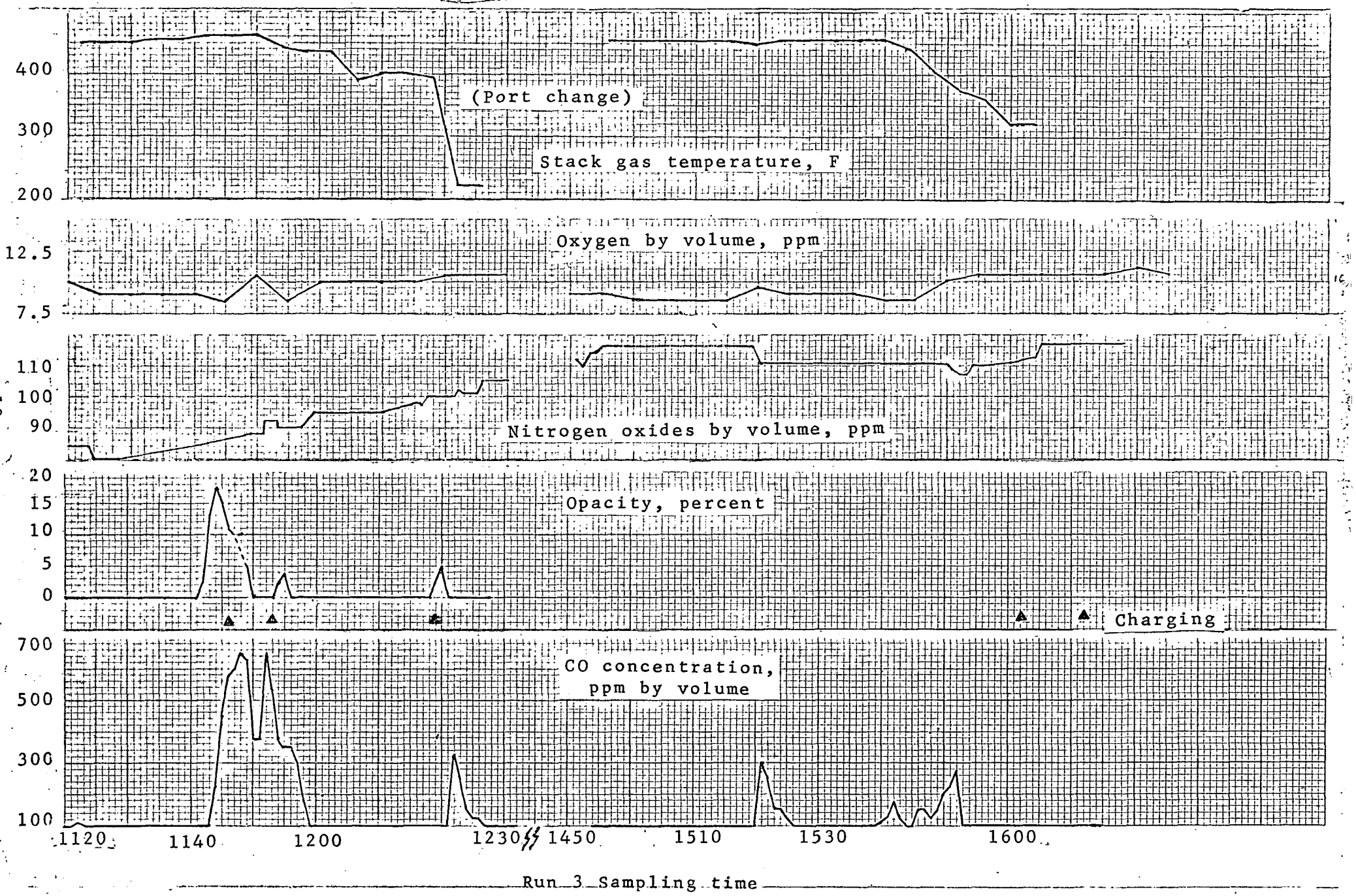


Figure 2.3. Graphic display of continuously monitored data.



than the continuous monitor recordings. The number of grab samples taken was not sufficient to determine if a true difference or apparent trend existed between the continuous monitor and the grab sample results.

CONTINUOUS NITROGEN OXIDES MONITORING

Nitrogen oxides concentrations, as measured by the continuous chemiluminescence method, ranged from a low of 80 ppm during Run 3 to a high of 130 ppm during Run 2 (Figures 2.1, 2.2, and 2.3). These concentrations appear to fluctuate independently of temperature, oxygen, carbon monoxide, and opacity.

CONTINUOUS OXYGEN MONITORING

The oxygen concentrations recorded by the continuous monitoring method ranged from a low of 8.5-percent during Run 3 to a high of 12.0-percent during Runs 1 and 2. These data correspond favorably to the oxygen levels measured by the Orsat method.

Oxygen levels remained relatively stable and appear to fluctuate independently of carbon monoxide, nitrogen oxides, opacity, and stack temperature fluctuations. Figures 2.1, 2.2, and 2.3 also display the recorded fluctuations of the oxygen levels.

CONTINUOUS CARBON MONOXIDE MONITORING

With the exception of spiking, which coincided with the regularly-occurring coke oven gas reversals, carbon monoxide measurements were generally below 300

ppm, and usually remained near zero. Carbon monoxide concentrations are graphically displayed in Figures 2.1, 2.2, and 2.3 for Runs 1, 2, and 3, respectively.

The two-way radios used by the C.F. & I. coke oven battery workers caused occasional "radio interference" problems with the NDIR analyzer, which limited the precision attainable from the strip chart recordings, especially in the concentration range encountered.

There seems to be no relative correlation between carbon monoxide and nitrogen oxides, oxygen, and temperature data. Stack gas opacity, however, seems to correspond with and closely track carbon monoxide fluctuations, thus a linear regression and correlation analyses were performed on the data.

Statistical Analysis of Data

The time-concentration curves (Figures 2.1, 2.2, and 2.3) were reduced in the following manner: The carbon monoxide strip chart continuous readings were reduced to 15-second point readings to correspond with discrete 15-second opacity readings. The CO readings were rounded to the nearest 100 ppm and those less than 100 ppm were interpreted to be less than the limit of detection. A data file was then created using corresponding opacity and CO readings at a given point in 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 for any given lag time. The lag time indicates the time, in minutes, before and after (negative or positive) an opacity reading to the associated CO reading. Each data file was then run through a linear regression program and correlation routine to determine if a significant relationship existed between the data for a given lag time. Different lag times were used to determine the optimum (maximum) correlation coefficient (r), beginning at whole minute intervals then reducing to quarter of a 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 CO readings but no associated 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 (defined by the maximum "r") and only complete data sets were utilized in the statistical analysis.

Results

Table 2.5 presents the results of the correlation analyses. A different time lag produced the optimum correlation coefficient (r) for each run (variation: -3.5 to 3 minutes). The results for each sample yielded a r-value of about 0.7. During the second half of Run 2, the CO readings were suspect due to very low readings, thus a second program iteration was made using only the first half of the test. This resulted in the much higher coefficient of 0.86. Appendix E presents the distribution of data pairs for each run.

Although continuous nitrogen oxide and oxygen data was available, the resolution of overall magnitude of oxygen concentrations was not sufficient to resolve the data over as many points as was needed. From the graphic summaries, however, no apparent trends seemed to exist. Therefore, this was the extent of the statistical analyses performed on this data.

Comparison with Previously Collected Data

The data from the C.F. & I. study was quite different than that previously collected at another battery stack location. Concentrations of carbon monoxide measured during

TABLE 2.5. SUMMARY OF CORRELATION RESULTS

Sample Number	No. of Data Sets	% of Data Used	Correlation Coefficient (r)	Linear Regression Equation	Lag Time, Minutes[a]
1	160	100	0.6802	CO = 29.6 op + 69.8	-3.5
2	271	100	0.6958	CO = 57.2 op + 121	2
	173[b]	100	0.8638	CO = 42.7 op + 114	
3	81	100	0.7403	CO = 24.4 op + 201	3

[a] Minutes from opacity reading to the carbon monoxide reading.
[b] Run using only the first half of the sample.

the earlier study ranged from 100 to 1500 ppm, while at C.F. & I. the greatest recorded concentration was 1100 ppm. Similarly, the maximum opacity at the other facility was 50-percent while at C.F. & I. the maximum was 20-percent, with most of the readings at 0-percent. As may be seen from the distribution of data pairs (Appendix E) for all runs, the majority of the readings at C.F. & I. were less than 150 ppm and either 0 or 5-percent opacity. This did not offer the wide variation in paired data sets as was present in the earlier study, thus outlying data sets did not suggest the need for elimination. Since no charge times were available as additional input, this relationship could not be explored for C.F. & I.

EXHAUST GAS COMPOSITION

Table 2.6 displays the results of the exhaust gas composition analysis using Method 3. Determinations of carbon dioxide, oxygen, and carbon monoxide content were made for each of the three sample runs. Moisture content is also presented and shows an average of 13.9-percent.

VISIBLE EMISSIONS

Visible emissions from the Battery D stack were recorded for the duration of each particulate sample run, with two exceptions. Readings were terminated

TABLE 2.6. EXHAUST GAS COMPOSITION ANALYSIS

Sample Number	Moisture Content percent	Exhaust Gas Composition, Dry Basis percent			
		Carbon Dioxide	Oxygen	Carbon Monoxide	Nitrogen and Inerts
1	13.8	4.2	9.1	<0.1	86.7
2	13.7	5.2	9.5	<0.1	85.3
3	14.2	4.9	10.7	<0.1	84.4
Average	13.9	4.8	9.8	<0.1	85.5

within minutes of the completion of Run 2 due to insufficient sunlight. Overcast conditions permitted about 1-hour of observation during Run 3.

The opacities recorded during these runs were consistently low, with the exception of occasional peaks and regularly occurring peaks which coincided with rises in carbon monoxide concentrations and with the coke oven gas reversals in Battery D. These reversals occurred every half-hour at approximately 20 and 50 minutes past the hour. The peaks in opacity occurred approximately four minutes following carbon monoxide peaks during Run 1 and three minutes prior to carbon monoxide peaks in Runs 2 and 3. Figures 2.1, 2.2, and 2.3 graphically depict the fluctuations in opacity during each run.

3.0 PROCESS DESCRIPTION AND OPERATION

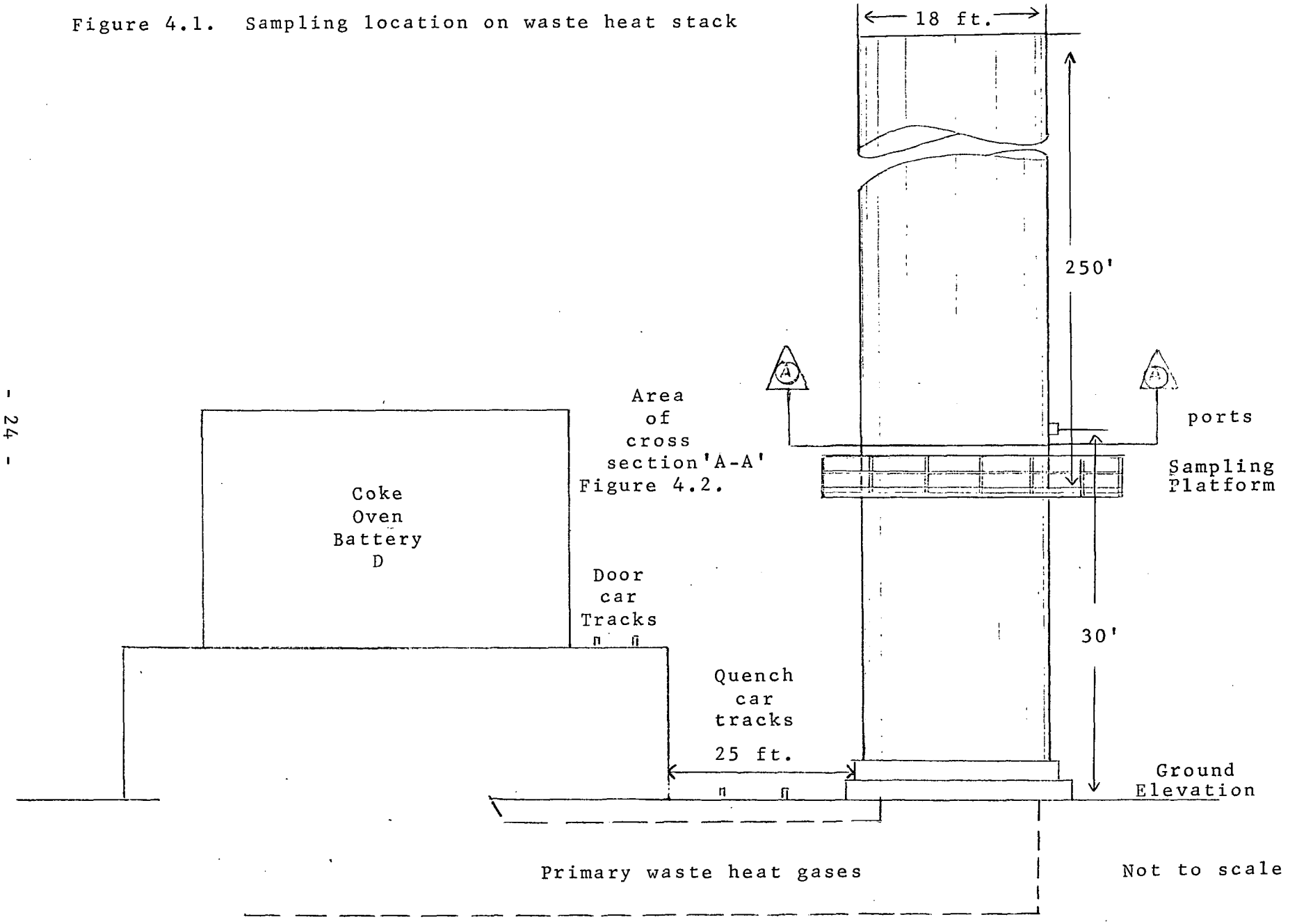
To be supplied by EPA.

4.0 LOCATION OF SAMPLING POINTS

At the sampling location elevation, access to the 10.2-foot I.D. waste heat battery stack was obtained through two of three sampling ports positioned approximately five stack diameters downstream from the underground, primary underfire flue duct and about 25 diameters upstream from the stack outlet. Two of the three ports had been previously installed through the four foot thick stack wall, at a 180-degree angle about the stack circumference, while the third port was installed perpendicular to these ports specifically for this testing program. Figure 4.1. characterizes the sampling location relative to the Coke Oven Battery D and stack. A total traverse of thirty-six sampling points, equally divided between two sampling ports spaced at 90 degrees, was employed during the testing program. Figure 4.2 depicts the location of each sampling point with respect to the inner stack wall.

The number of sampling and traverse points chosen afforded suitable velocity traverse data, considering the very low (natural draft) flowrates. The four outermost traverse points' sampling times were incorporated into the next inwardmost points due to their

Figure 4.1. Sampling location on waste heat stack



Point Number	Distance from wall	
	inches	cm
1	1.7	4.4
2	5.4	13.7
3	9.2	23.3
4	13.3	33.9
5	17.9	45.5
6	23.0	58.4
7	28.9	73.4
8	36.2	92.0
9	46.8	118.8
10	75.6	192.1
11	86.2	218.9
12	93.5	237.5
13	99.4	252.5
14	104.5	265.4
15	109.1	277.0
16	113.2	287.6
17	117.0	297.2
18	120.7	306.5

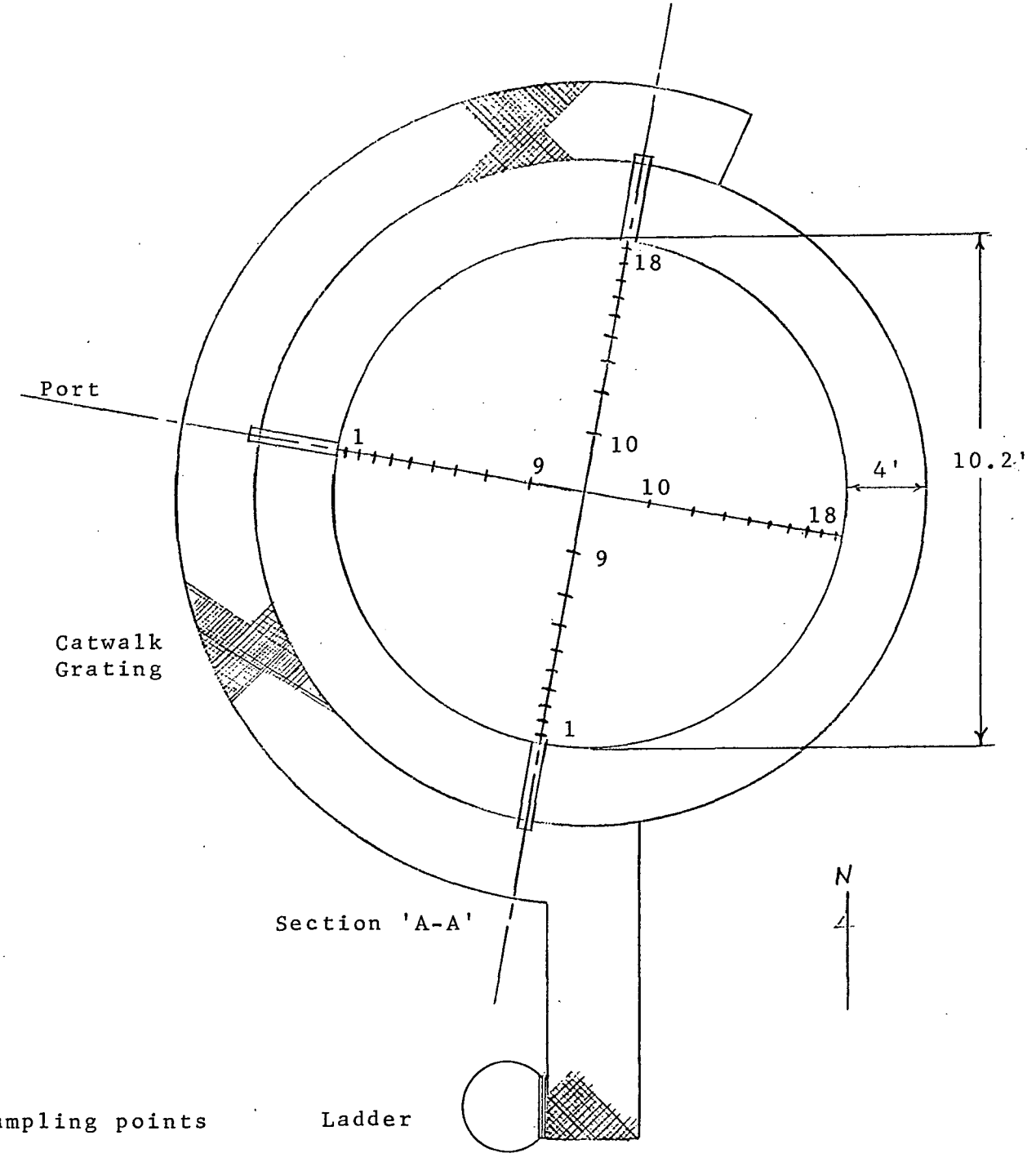


Figure 4.2. Location of sampling points

being positioned too close to the stack port liners to obtain representative velocity pressures. These port liners were not flush with the stack inner wall.

Throughout the testing program, difficulty was encountered when changing ports and with the support of the 16-ft probe. When the probe was largely outside of the stack, its weight placed considerable pressure on the front part of the probe, forcing the total length of the probe to bow. This bowing eventually caused the nozzle to catch the inside of the stack wall, making the probe intractable unless first disassembled. This problem precipitated the modification of the sampling nozzle after completion of the first test. With the approval of the EPA Technical Manager, a portion of the "elbow" type nozzle tip was removed and re-tapered. This allowed removal of the probe from the port without disassembly.

5.0 SAMPLING AND ANALYTICAL PROCEDURES

A detailed summary of sampling and analytical procedures is presented in Appendix F. Calibration data is included in Appendix G.

PARTICULATE SAMPLING

Prior to particulate sampling of the waste heat exhaust stack, preliminary determinations were made to select a sampling nozzle of proper size to maintain isokinetic sampling rates throughout the sampling study. During these preliminary determinations the following were executed:

(1) The establishment of a minimum number of sampling points for the sampling site, calculated according to Method 1;

(2) The measurements of the stack static pressure, stack velocity pressure profile and temperatures at each sampling point, per Method 2 procedures;

(3) Determination of the stack gas dry molecular weight as described in Method 3; and,

(4) the approximate stack gas moisture content using Method 4.

While conducting the moisture test, the metering system (i.e., the vacuum pump vanes) malfunctioned

and was unable to maintain a steady flowrate for the remainder of the test. This preliminary test resulted in a moisture value of 3-percent, which was 10-percent lower than the average moisture value from a previous testing program for this source. The approximate moisture content thus determined was deduced to be suspect. Therefore, the average moisture value (13-percent) from previous battery stack emission studies was used for the preliminary determination of the isokinetic sampling rate. This assumed moisture value turned out to be 0.9-percent below the average actual percent moisture data for this emission study.

Triplicate 144-minute particulate samples were extracted isokinetically for 4-minutes at each of 32 of the 36 sampling points in the waste heat stack. Points 1 and 18 on each traverse diameter were judged to be too close to the sampling port liners, which were not flush with the stack wall, so points 2 and 17 were sampled for twice the normal duration, thus deleting four sampling points.

As it would have been difficult to support and move an impinger box at the end of a 16-foot probe it was necessary to modify an EPA Method 5 particulate sampling train. The heated filter was placed at the end of the probe and connected to the impingers with a flexible Teflon® line (Figure 5.1.). The sampling train consisted

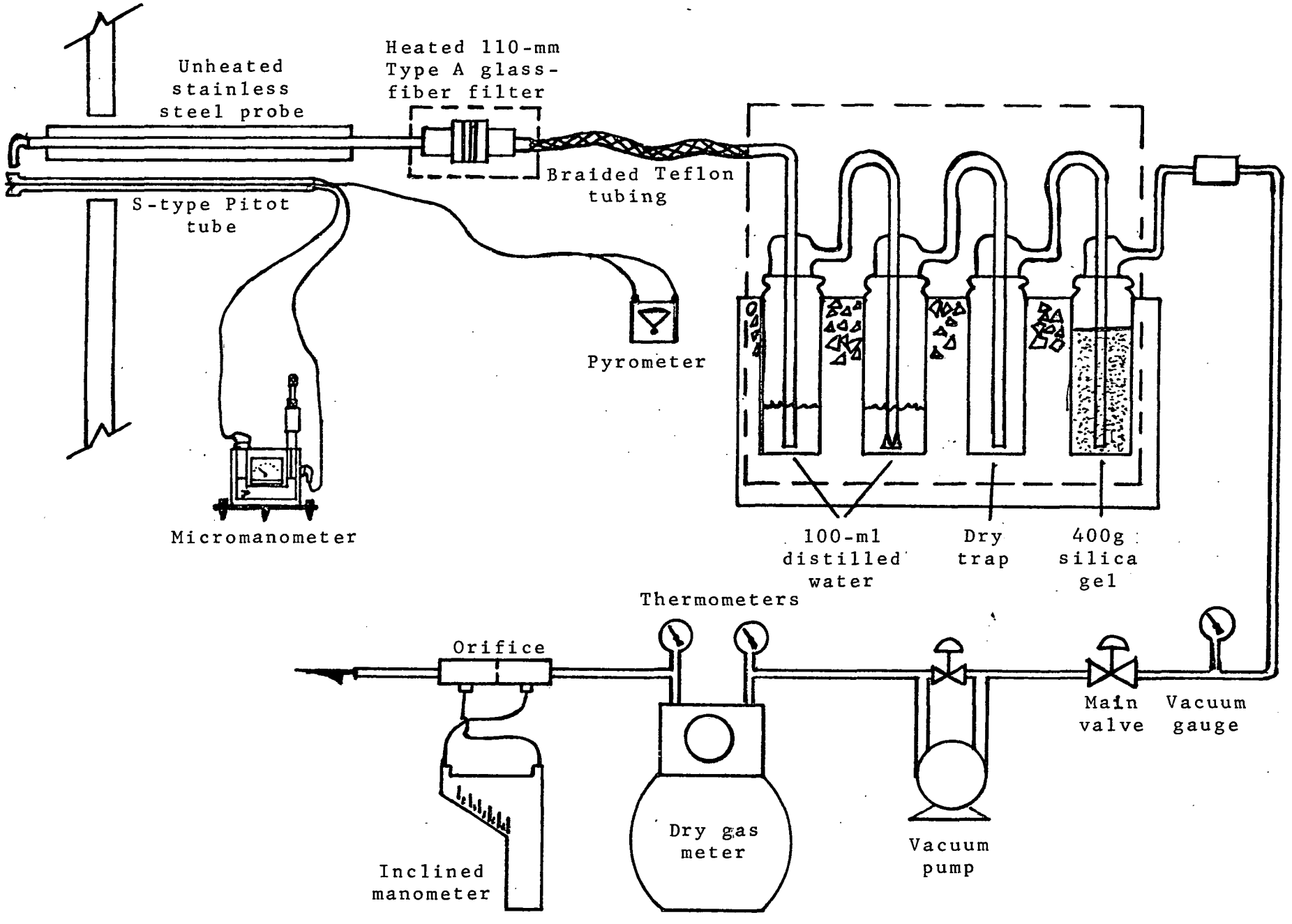


Figure 5.1. Particulate sampling train.

of (in sequential order of sampled gas flow): a sharp, tapered, stainless steel (SS) sampling nozzle; a 16-foot SS probe assembly (instead of a glass probe, due to the obvious probability of breakage during testing); a heated, pre-weighed 110- millimeter (mm) Type-A glass-fiber filter; flexible Teflon® tubing leading to two Greenburg-Smith impingers, the first modified, the second standard, each containing 100-milliliters (mls) 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 connected to a zero to ten-inch range inclined (water gauge) manometer.

The impinger train was immersed in an ice bath to maintain the temperature in the last impinger at 70F or less. A calibrated S-type Pitot tube was connected to the sampling probe and velocity pressures were read on a zero to two-inch micro-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 probe and filter temperatures were kept above the dew point of the exhaust gases sampled.

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 cfm at 15-inches of mercury vacuum and the final leak rate shall not exceed 0.02 cfm at the greatest vacuum which occurred during the test.

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, using an orifice-type meter to indicate instantaneous flowrates.

Following the leak check at the end of each 144-minute sample run, the sampling train was transferred to a sheltered clean-up area. The volumes of the impinger contents were measured and volume increases recorded. The solutions were placed in glass sample bottles and sealed with Teflon®-lined caps. The silica gel was weighed to determine the weight gain (as condensate). The probe and nozzle assembly was initially rinsed and brushed with water and then with acetone.

The two rinsings were collected in separate glass sample bottles with Teflon®-lined caps. The impinger assembly was thoroughly rinsed with water, and these water rinsings were placed with the impinger solutions. Following the water wash of the impingers, the entire impinger assembly was then rinsed with acetone and these rinsings were placed in separate glass sample bottles and sealed with Teflon®-lined caps. The glass-fiber filter was carefully returned to its original petri dish and sealed for transport. The front half of the filter holder was rinsed and brushed with water and acetone and these rinsings were added to the probe rinses. The back half of the filter holder and the Teflon® flexline were rinsed and brushed with water and acetone, and these rinsings were added to the contents and rinsings of the impingers. Thus, five fractions were collected from each sample run:

(1) water washings of nozzle, probe and front half of filter holder;

(2) acetone washings of nozzle, probe and front half of filter holder;

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

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

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

In the laboratory, all liquid fractions were observed for leakage, then each measured volumetrically and the values recorded.

PARTICULATE EMISSIONS

A 50-ml aliquot was removed from Fractions 1 and 4 prior to the particulate analyses for sulfate analysis. The Fraction 1 samples were then transferred to tared beakers and evaporated to dryness at 105C. The dried residues were desiccated for at least 24 hours before determining constant weights. (A constant weight is determined by redesiccating the sample for at least 6-hours and then reweighing it. A difference between these weights less than 0.5 milligram, or 1-percent of the total weight, constitutes a constant weight.) The acetone volumes of Fractions 2 and 5 were transferred to tared beakers, evaporated to a residue at ambient conditions, then desiccated for 24-hours before constant weights were determined. The 110-mm Type A filters were desiccated at ambient conditions for more than 24 hours to determine constant weights.

The particulate and sulfate weights by fraction are presented in Appendix H.

Chloroform/Ether Extraction

After sulfate aliquots (50-ml) were removed, Fraction 4 water samples were extracted three times with equal volumes (30-ml) of chloroform and ethyl ether (C/E). The organic phases (C/E extractables) of each sample were collected and combined in separate tared beakers, evaporated to dryness at ambient conditions, and desiccated for 24 hours before constant weights were determined. The remaining water phase of Fraction 4 samples were evaporated to dryness at 105C, desiccated 24 hours and measured to constant weights. The sum of the C/E extractable organic weight and the aqueous phase weight (inorganic fraction) is the total weight of Fraction 4.

Sulfate Analysis

The 110-mm filters (Fraction 3) were leached of sulfates by liquefying each filter with 80-percent isopropanol (IPA) in a blender, scrubbing the amalgamated solutions in an ultrasonic bath, punctually followed by filtering the solutions and diluting the filtrate to 150 mls with 80-percent IPA. The residues from Fractions 2 and 5 were leached of sulfates by scrubbing the residue with 80-percent IPA in an ultrasonic bath then bringing to 100-ml volume with 80-percent IPA. Five-ml portions

of 50-ml aliquots of Fractions 1 and 4 were brought to 25-ml volumes with 100-percent isopropanol to form 80-percent solutions.

Each of the above solutions was adjusted for acidity with perchloric acid to a pH between 2.5 and 4.0. Three to five drops of thorin indicator were added to each solution before titrating with standardized barium perchlorate to a pink endpoint. The results are reported as sulfuric acid (including sulfur trioxide) and as a percent of the particulate weight for the individual fractions.

Exhaust Gas Composition

An integrated gaseous sample was withdrawn simultaneously with each particulate sample from the south port of the waste heat stack. The Orsat sampling train utilized during the first two sample runs consisted of a SS probe; a particulate/condensate trap; a leakless diaphragm pump; a pressure release connection; a needle valve coupled with a rotameter; and a 96-liter Saran® sample bag. All intermediate connections were made with lengths of polyvinylchloride (PVC) tubing. See Figure 5.2 for a graphic display of the sampling train used in gaseous sampling.

The Orsat sampling train was modified for Run 3, in that the carbon monoxide (CO) sampling

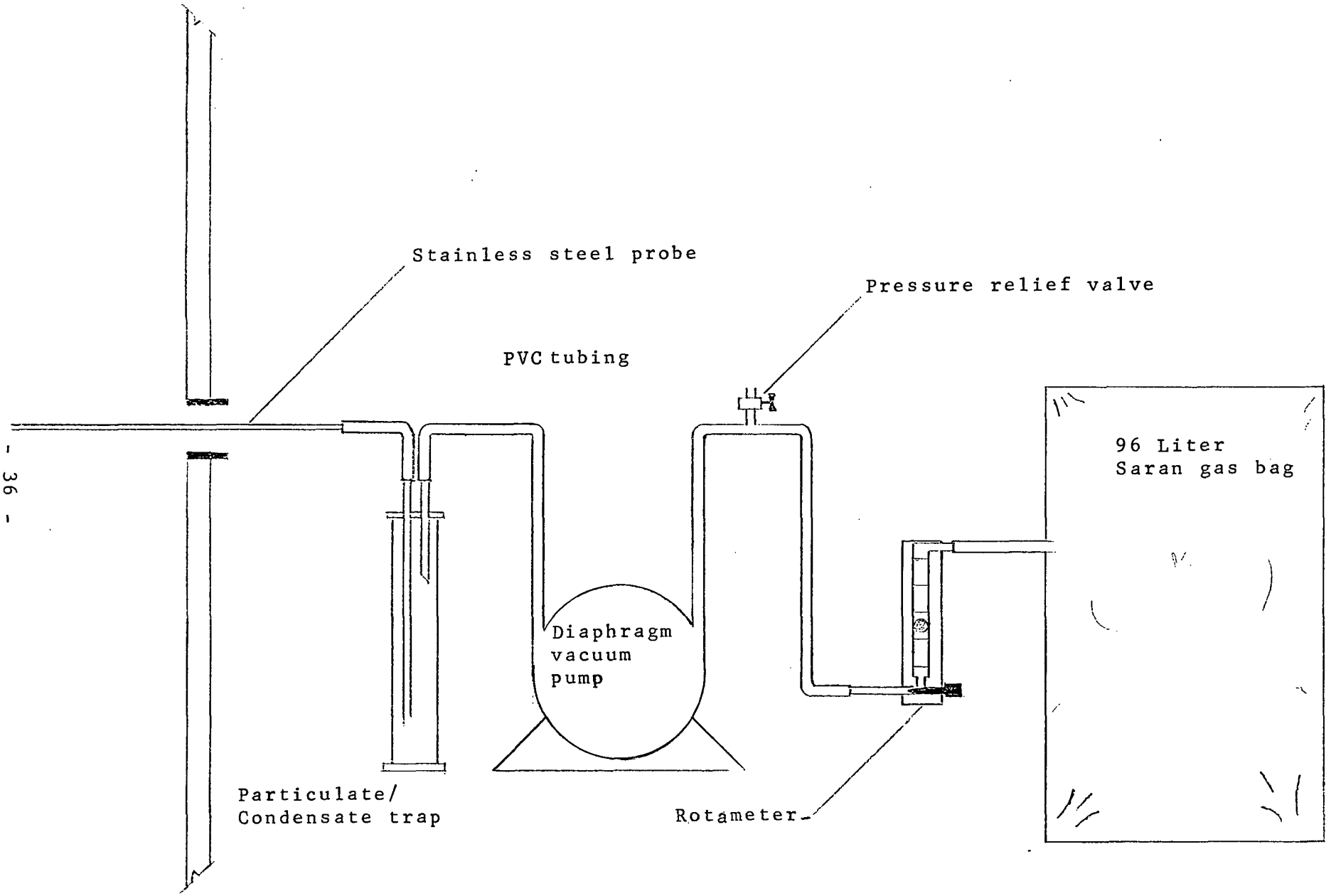


Figure 5.2. Orsat gas sampling train.

probe, particulate/condensate trap, and intermediate Teflon® tubing replaced their counterparts from the previous Orsat train. In addition,a 3-way brass valve was inserted after the particulate/condensate trap to split the gaseous sample for both continuous CO monitoring and integrated bag sample collection.

Each integrated bag sample was analyzed by the Orsat method for carbon dioxide, oxygen and carbon monoxide concentrations as specified in EPA Method 3. The results were used to calculate the molecular weight of the waste heat exhaust gas in the Battery D stack.

CARBON MONOXIDE SAMPLING

A sample of flue gas was drawn through a SS probe, Teflon® tubing and a particulate/condensate trap containing glass wool, to a pair of modified Greenburg-Smith impingers. The first impinger contained approximately 250 grams of silica gel and the second approximately 500 grams of Ascarite® to remove moisture and carbon dioxide, respectively. Finally, a leak-free diaphragm pump forced the sample through a needle valve and rotameter to a Beckman, Model 865, NDIR Analyzer.

The sampling probe was positioned in the west port of the stack for the first and second particulate runs but was moved to the south port for Run 3.

The sampling train was modified for the third sample run to accommodate the simultaneous collection of an integrated bag sample for the determination of exhaust gas composition by the Orsat method. The modification consisted of inserting a 3-way brass valve after the particulate/condensate trap, which was used to divide the gas sample into two streams, one for the Beckman NDIR Analyzer and the other for the Orsat integrated gas sample.

At the sample interface to the Beckman NDIR Analyzer, an approximate flowrate and delivery pressure of 1.5 cfh and 10 psig respectively, were maintained for the duration of continuous sampling. An analog strip chart recorder was used to record all instrument outputs. This sampling system is depicted in Figure 5.3.

The daily calibration sequence included passing a certified standard zero gas (dry nitrogen) and a certified standard span gas concentration (carbon monoxide in nitrogen) through the analyzer. The instrument output was calibrated for the anticipated range of 0 to 10,000 ppm carbon monoxide by adjustment of the zero and gain levels to the appropriate signal, as indicated on a calibration curve. Following the analyzer calibration, the strip chart recorder pen response was increased by a factor of ten by changing its input range.

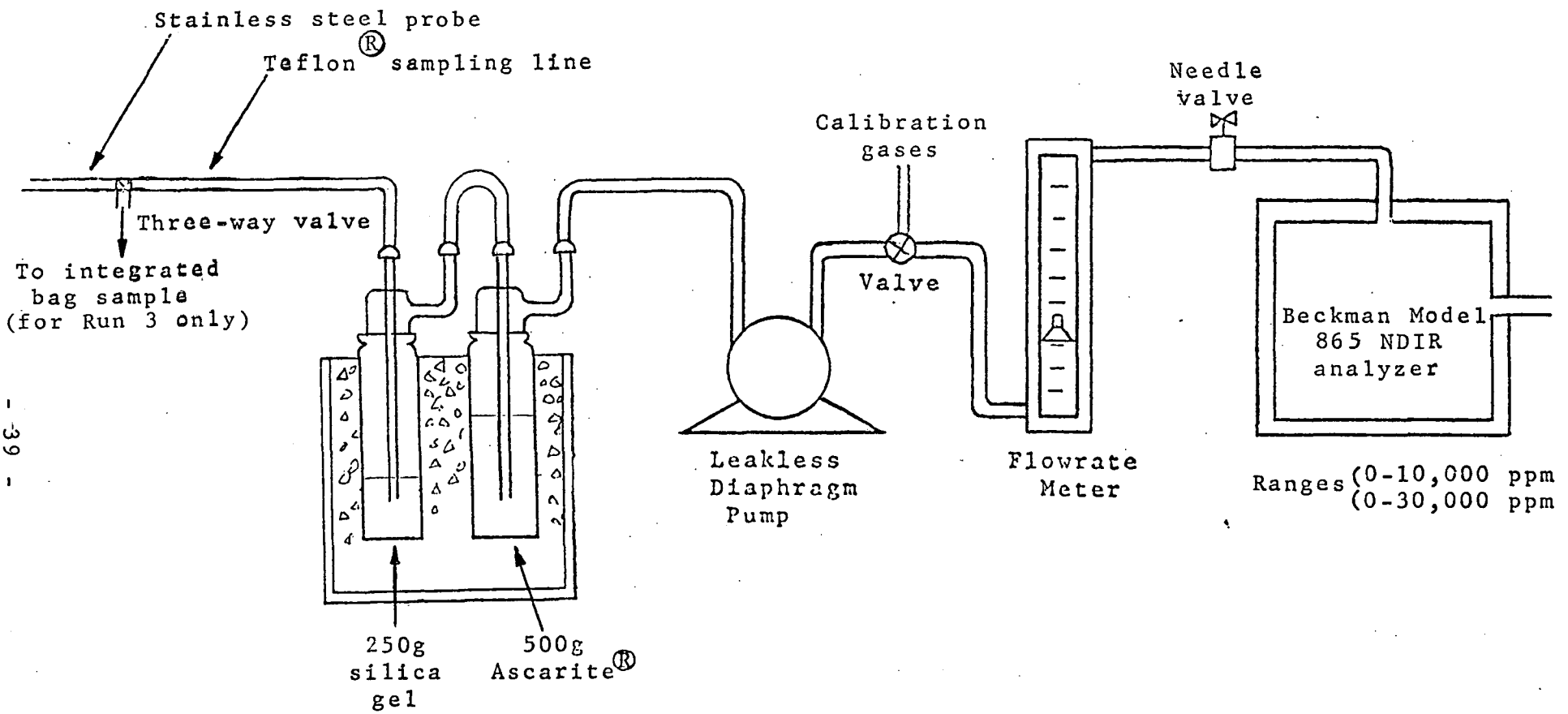


Figure 5.3. Sampling train for continuous monitoring of carbon monoxide.

The Beckman NDIR analyzer, which operates by the Luft principle specified by Reference Method 10, was equipped with a four-position valve to allow the introduction of sample gas or any of the required standard calibration gases, as depicted in Figure 5.3.

The actual measured concentrations of carbon monoxide 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.

COMBINATION SAMPLE EXTRACTION SYSTEM FOR NITROGEN OXIDES AND OXYGEN

An in-stack stainless steel (SS) alundum thimble holder, packed with glass wool, was positioned in the North port of the D Battery stack throughout the complete testing study. The intermediate connections between components were accomplished using lengths of Teflon® tubing. A three-way SS valve was incorporated in-line after the probe to branch off to a leakless diaphragm pump. The 3-way valve facilitated sampling system leak checks and back purging of the probe assembly. Subsequently, the sampled gas flowed into an ice-cooled condenser and through a leakless diaphragm pump.

A SS control valve maintained the gas flow at 2 $\pm$ 0.5 scfh at the outlet of the rotameter downstream of both analyzers. A pair of SS "tee" connectors allowed aliquots of gases to be bled off to the analyzers. See Figure 5.4 for the schematic of the continuous extraction system and NO_x-O_2 analyzers.

A leak check of the system was performed prior to each day's testing by closing the 3-way valve following the probe assembly and observing the deflection of a rotameter at the outlet of the sampling system. Any noticeable deflection after a 2-minute time period indicated a leak in the sampling system.

CONTINUOUS NITROGEN OXIDES MONITORING

An aliquot of exhaust gases was withdrawn from the "tee" connector through a 3-way SS valve to a Thermo-Electron NO_x Analyzer. The sampled gas flow through the NO_x analyzer was monitored and maintained at 2.5 scfh by means of a flow meter mounted on the panel of the analyzer. Ambient air (dried) was employed as an oxygen source for the ozone generator within the analyzer. The vacuum pressure to the reaction chamber was monitored by a gauge connected with the chamber unit. The analyzer output signal was connected to a linear strip chart recorder which was set at a chart speed of 0.5 centimeters/minute (cm/min).

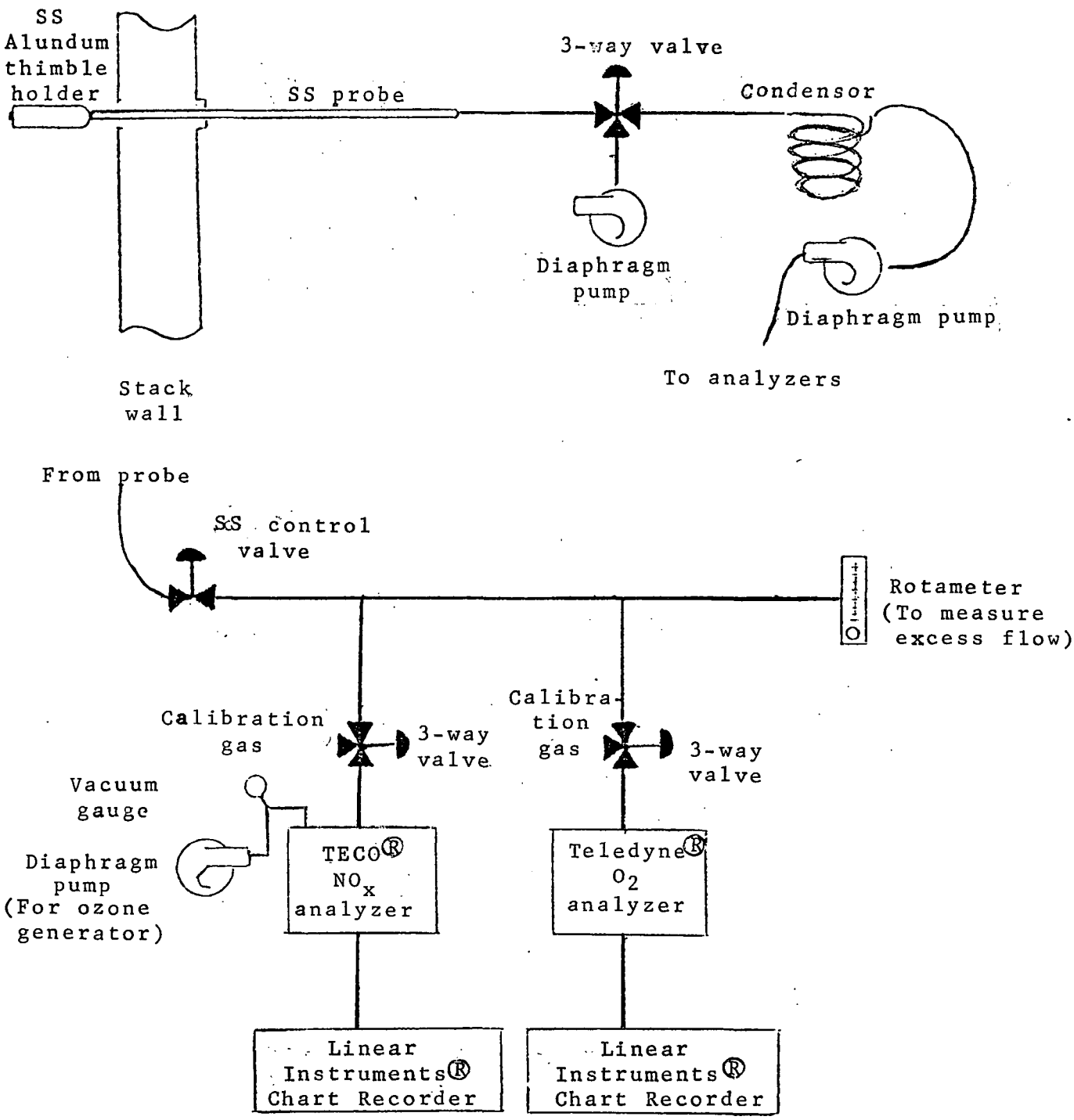


Figure 5.4. Combination sampling trains for continuous monitoring of nitrogen oxides and oxygen.

Calibration checks were performed prior to the start-up of each run, at selected times during testing, and at the completion of each day's testing.

CONTINUOUS OXYGEN MONITORING

A separate aliquot of the exhaust gases was withdrawn from the "tee" connector through a 3-way SS valve to a Teledyne Model 326A Oxygen Analyzer. The flowrate was continually maintained at 2 to 2.5 scfh throughout the testing program. The analyzer output signal was connected to a linear strip chart recorder with a chart speed of one-inch per hour. Calibration checks were routinely performed.

NITROGEN OXIDES GRAB SAMPLES

Daily "grab samples" were acquired from the waste heat stack for nitrogen oxides analysis, according to EPA Method 7. The nitrogen oxides sampling train apparatus is depicted in Figure 5.5. The field data for each sample is included in Appendix B-3.

After evacuating each flask containing dilute sulfuric acid/hydrogen peroxide absorbing solution to the appropriate vacuum pressure and leak checking, the SS probe and glass stopcock were purged with stack gas for approximately one minute. The stop-cock was then returned to the sampling position for

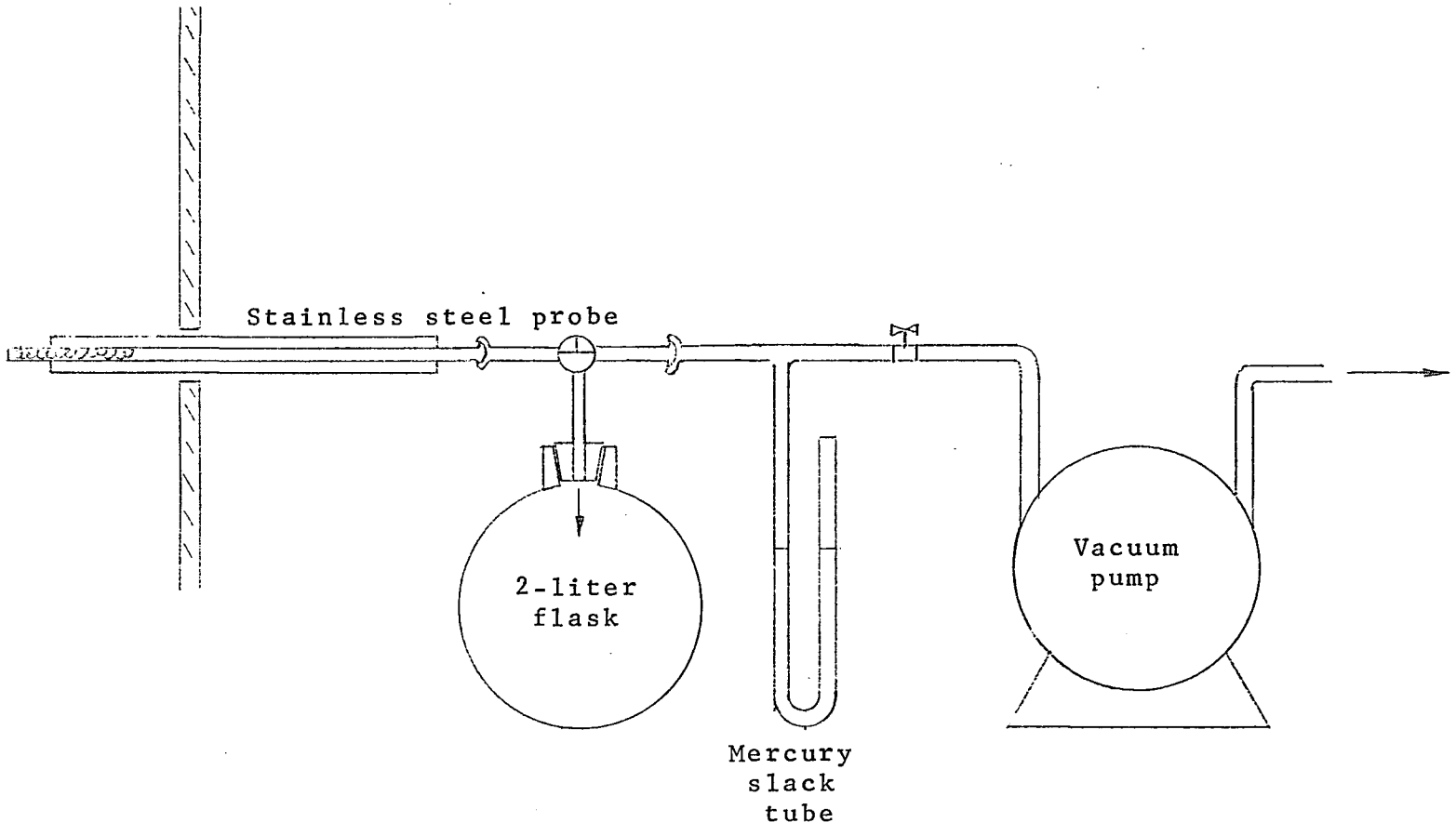


Figure 5.5. Sampling train for nitrogen oxides grab samples.

a period of approximately thirty seconds to insure equal pressurization between the sampling system and stack gases. Immediately following sample collection, each flask was shaken for five minutes and stored for at least 16 hours away from sunlight.

Prior to sample recovery, each flask was shaken for two minutes, followed by the measuring and recording of the internal pressure and temperature of the flask. The contents of each flask were transferred to leak-free polyethylene bottles along with two 5-ml water rinses. The pH of each solution was adjusted to a range of 9 to 12 with 1.0 N. sodium hydroxide before the bottles were marked, labelled and sealed for transport to the laboratory.

In the laboratory, the sample bottles were examined for leakage before transferring their contents to tared beakers along with sample bottle water rinsings. The samples were evaporated to dryness and treated successively with solutions of phenol disulfonic acid, distilled water, and sulfuric acid. The resulting solution was made basic with ammonium hydroxide, transferred to a volumetric flask, and diluted to volume with distilled water. The standard wavelength absorbance at 410 nanometers was measured and recorded as nitrogen dioxide in the samples and potassium nitrate standards.

VISIBLE EMISSIONS

Visible emissions from the D Battery stack exhaust were recorded for the duration of each sample run except for Run 3, for which visible emissions recording was 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

BαP SAMPLING AND ANALYSIS

The sampling train used to collect BαP was identical to the particulate train except the BaP train contained an absorbent module between the filter and the first impinger.

The module was packed with a polymeric absorbent, XAD-2 (styrene divinyl benzene). The temperature of water circulating through the cooling jacket was maintained at 127°F, therefore, the sampled gas would pass through the adsorbent material at a constant cooled temperature. The adsorbent module was covered with aluminum foil throughout the testing to prevent deterioration of the sample from exposure to ultraviolet light. The described operation of the absorbent module was the only variance of the BαP train from the particulate train.

The moisture content of the stack gas must take into account all the water collected in the BαP train. The water collected in the impingers and silica gel will not accurately reflect the true moisture content of the stack gas as the adsorbent module is located immediately behind the heated filter and water cooled to 127°F; this temperature change will cause condensation of the stack gas in the middle before the impingers. Therefore, in operating a BαP train at a source with a high moisture content, either a moisture train or a Method 5 train should be operated during the run. This would provide an accurate moisture determination for the BαP run. This test utilized the moisture content from the Method 5 train as the source for BαP data reductions.

CF & I Battery Outlet

BαP - Test Results

RUN	1	2	3	Average
DATE	8-7-79	8-8-79	8-9-79	
Meter Volume (DSCF)	46.26	95.34	81.92	74.51
Meter Volume (DSCM)	1.31	2.70	2.32	2.11
Stack Volume (ACFM)	22,060	19,280	19,976	20,438
Stack Volume (DSCFM)	10,032	8,460	8,820	9,104
Stack Volume (DSCMM)	284.1	239.6	249.8	257.8
% Isokinetic	104.0	125.1	108.8	112.6
mg/Filter	0.350	0.350	0.200	0.300
mg/Rinse	11.288	7.236	11.618	10.047
mg/XAD-2	0.725	0.300	1.200	0.742
mg/Total	12.363	7.886	13.018	11.089
mg/DSCM	0.0094	0.0029	0.0056	0.0060
kg/Hour	0.0002	0.00004	0.00008	0.00009
lbs/DSCF	58.68×10^{-11}	18.10×10^{-11}	34.96×10^{-11}	37.45×10^{-11}
lbs/Hour	3.532×10^{-4}	9.188×10^{-5}	1.850×10^{-4}	2.046×10^{-4}
lbs/24 Hour Day	8.48×10^{-3}	2.20×10^{-3}	4.440×10^{-3}	4.910×10^{-3}
lbs/365 Days	3.10	0.80	1.62	1.79