

AIR POLLUTION EMISSION TEST

CABOT CORPORATION

Waverly, West Virginia

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Emission Measurement Branch
Research Triangle Park, North Carolina

FINAL REPORT

on

SAMPLING AND ANALYSIS OF SOURCE EMISSION
SAMPLES FROM A CARBON BLACK PLANT

to

ENVIRONMENTAL PROTECTION AGENCY

May 12, 1975

by

S. E. Miller and R. E. Barrett

EPA Contract No. 68-02-1409
Task Order No. 9

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
Summary and Conclusions	2
Plant and Process Detail.	4
Sampling Locations.	4
Total Stack Flow	7
Sampling and Analytical Procedures.	7
Particulate and POM.	7
Sample Recovery.	9
Analysis for POM Species	11
Hydrogen Sulfide (H ₂ S) by Method 11.	14
Sulfur Dioxide (SO ₂) by Method 6	14
Hydrocarbons and Reduced Sulfur Compounds.	17
Carbon Monoxide (CO), Carbon Dioxide (CO ₂) and Oxygen (O ₂).	20
Moisture	20
Visible Emissions.	22
Infrared Telespectrometer Measurements	22
Recommendations on Sampling Procedures.	22
H ₂ S - EPA Method 11.	22
SO ₂ - EPA Method 6	24

APPENDICES

- APPENDIX A. PROCESS DESCRIPTION
- APPENDIX B. INFRARED REMOTE SENSING MEASUREMENTS
- APPENDIX C. FIELD DATA FOR VISUAL DETERMINATIONS
 - FIELD DATA FOR METHOD 5 POM RUNS
 - FIELD DATA FOR "PACKED COLUMN" POM RUNS
 - SO₂ AND H₂S TITRATION DATA

List of Tables

	<u>Page</u>
Table 1. Summary of Emissions from a Carbon Black Plant	3
Table 2. Total Stack Gas Flow	8
Table 3. Particulate Data Unit No. 3.	10
Table 4. Summary of Hydrogen-Sulfide Data - EPA Method 11	15
Table 5. Summary of Sulfur Dioxide Data - EPA Method 6.	16
Table 6. Summary of Results - Gas Chromatography, Mass Spectrometry.	18
Table 7. Summary of Results - Gas Chromatography, Mass Spectrometry.	19
Table 8. Summary of Orsat Data.	21
Table 9. Summary of Visible Emissions	23

List of Figures

Figure 1. Flow Diagram, Cabot Carbon Black Plant.	5
Figure 2. Stack Geometry and Sampling Port Locations.	6

SAMPLING AND ANALYSIS OF SOURCE
EMISSION SAMPLES FROM A CARBON-BLACK PLANT

by

S. E. Miller and R. E. Barrett

INTRODUCTION

This report summarizes the results of a sampling program recently conducted at the Cabot Corporation "Ohio River" carbon-black plant in Waverly, West Virginia. The program was conducted by Battelle-Columbus pursuant to the terms of Task Order No. 9, Contract No. 68-02-1409 with the U.S. Environmental Protection Agency.

The objective of this program was to obtain accurate and detailed data on air pollutant emissions from the Cabot Corporation Waverly plant for the Standard Support Document for the Carbon-black industry.

The field-sampling portion of the program was conducted during the week of December 9-13, 1974. Battelle's Columbus Laboratories (BCL) was responsible for measuring gas compositions in the stack upstream of the flares (i.e., below the flares) for Polycyclic Organic Matter (POM), H_2S , SO_2 , CO, and selected hydrocarbons. In addition, Battelle measured CO_2 , O_2 , and moisture content of the gas and visible emissions. Concurrent with the BCL measurements, EPA used an infrared telespectrometer system to obtain remotely emission spectra of flare species over the spectral range of 2 to 14 microns. Operation of the plant and control systems were monitored by PEDCO-Environmental of Cincinnati, Ohio, who are also under contract to EPA to develop information for the emission standard support document.

Because the sampling described in this report was conducted upstream of the flare, the measured values of combustible species (CO, hydrocarbons, and POM) should not be considered as equivalent to emissions. Actual emissions of CO and hydrocarbons would be less than the measured values. Actual emissions of POM are impossible to estimate based on the current knowledge of POM reactions.

The initial sampling and analysis schedule for this task called for BCL to obtain 2 gas samples from each of the 3 process trains. However,

during the field-sampling period, Unit No. 1 was not in operation due to periodic maintenance and installation of new bags in the baghouse. Consequently, the sampling schedule was changed to include 3 samples from each of Units No. 2 and No. 3. The sampling operation was conducted as four separate runs with multiple samples obtained during some runs. The run schedule was as follows:

Run No. 1	Unit 3	December 10 (velocity profile obtained December 9)
Run No. 2	Unit 3	December 11
Run No. 3	Unit 2	December 11
Run No. 4	Unit 2	December 12
Run No. 5	Unit 3	December 12 (POM run only)

Multiple samples obtained during one run are identified by postscripts on the run numbers (e.g., 5A, 4B).

Summary and Conclusions

Table 1 summarizes results of the gas composition measurements made by BCL at the Cabot carbon-black plant.

Upstream of the flare (in the stack) the exhaust gas from this source is incompletely oxidized and, hence, at the point at which sampling was conducted the majority of the sulfur is present in reduced species (H_2S and CS_2) rather than as SO_2 . Based on the mass spectrometer data, if all the reduced sulfur compounds were oxidized to SO_2 in the flare, the equivalent emission of SO_2 would be:

Run No. 1	62 to 65 Kg SO_2 /hr equivalent
Run No. 2	100 to 103 Kg SO_2 /hr equivalent
Run No. 4	100 to 103 Kg SO_2 /hr equivalent.

Some disagreement is observed in the H_2S data acquired by Method 11 and by mass spectrometer analysis. As discussed elsewhere in this report, the large concentrations of H_2S present in the stack gas were beyond the normal range of Method 11. Also, interference reactions with other sulfur compounds present in the stack gas are suspected. Hence, the mass spectrometer values were accepted as more accurate.

TABLE 1. SUMMARY OF GAS COMPOSITIONS MEASURED UPSTREAM OF THE FLARE AT A CARBON-BLACK PLANT

	Run Number				
	1	2	3	4	5 ^(a)
	Unit Number				
	3	3	2	2	3
Gas Analysis, volume percent					
CO ₂	--	3.7	--	3.1	--
O ₂	--	0.5	--	0.8	--
CO	--	13.3	--	13.3	--
Moisture, vol percent	43	45	48	45	--
Total Dry Gas Flow Rate in Stack Nm ³ /min	327	336	429	378	--
Total Gas Flow Rate at Sampling Point C, Nm ³ /min	38.3	38.4	--	--	38.9
Flow of Specific Species, kg/hr					
SO ₂ (Method 6)	0.38	--	--	4.83	--
SO ₂ (GC)	< 2.6	< 2.6	--	< 3.0	--
H ₂ S (Method 11)	18.2	38.3	31.0	38.0	--
H ₂ S (GC)	19.4	22.8	--	18.2	--
CS ₂ (GC)	12.4	31.9	--	35.8	--
COS (GC)	4.4	3.2	--	4.9	--
H ₂ (GC)	276	284	--	267	--
CH ₄ (GC)	86.1	92.6	--	68.6	--
C ₂ H ₂ (GC)	250	260	--	307	--
C ₂ H ₄ (GC)	7.8	8.2	--	4.3	--
C ₂ H ₆ (GC)	< 0.1	< 0.1	--	< 0.1	--
Total C ₃ and C ₄ hydrocarbons (GC)	4.3	5.0	--	5.6	--
Total POM (Packed Column)	0.00030	--	--	--	--
Opacity, percent	--	8.8	13.8	--	--

(a) This run made for POM only.

Measurement of carbon monoxide (CO) was attempted by non-dispersive infrared (Method 10), but levels were far in excess of the limit of the available instrument (6000 ppm). CO determinations were made by two alternate methods, i.e., EPA Method 3 (Orsat) and gas chromatography.

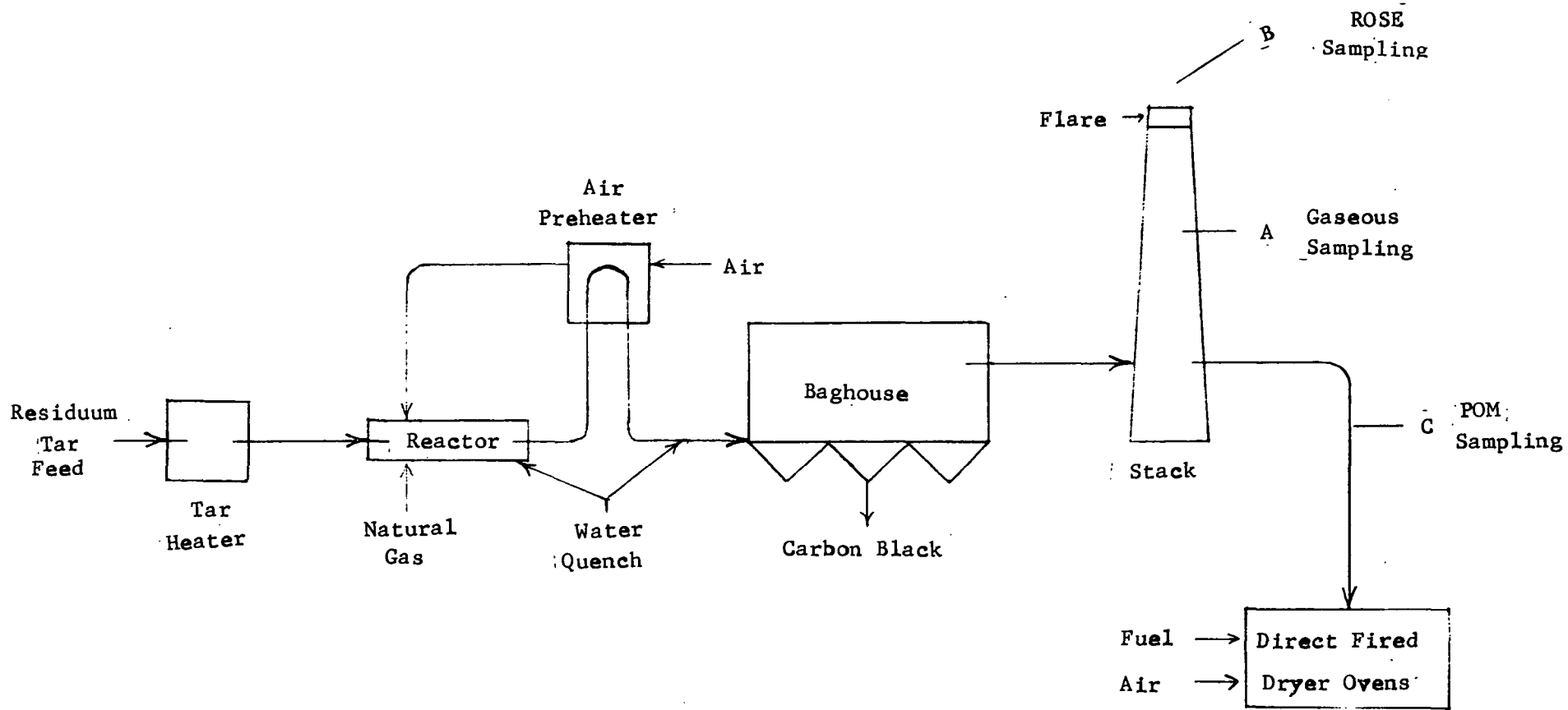
Plant and Process Details

The Cabot Ohio River plant contains 3 process units where carbon black is produced from residium tar. A process-train flow diagram is shown schematically in Figure 1. Each process train is equipped with a separate baghouse for collecting the carbon-black product and atmospheric flares for disposal of off gases. The plant has a vertically oriented design with the reactor effluent going to the baghouses at the top of the structure and the carbon black passing to successively lower levels for each processing step. A portion of the flue gas (about 13 to 15 percent) from one train is returned as auxiliary fuel for the direct-fired dryer ovens.

During the field-sampling period, process operations at the Cabot Ohio River plant were maintained at normal operating levels on Units 2 and 3 while Unit 1 was out of service. No major upset or change in operating condition was encountered during the sampling periods. During the last day of sampling, the flares on Unit 2 were turned off and could not be re-ignited because of high winds. This should have no significant effect on the BCL stack sampling results since the sampling port for this unit was located 10 feet below the flares. Further details on this process and an operations log have been provided by PedCo and appear in Appendix A.

Sampling Locations

Stack geometry and sample-port locations are shown in Figure 2. Integrated gas samples were extracted from the main stacks approximately 10 feet below the flares (Point A). Particulate measurements for POM (polycyclic organic matter) determinations were made at a lower level take-



NOTE: The plant has three of these trains.

FIGURE 1. FLOW DIAGRAM, CABOT CARBON BLACK PLANT

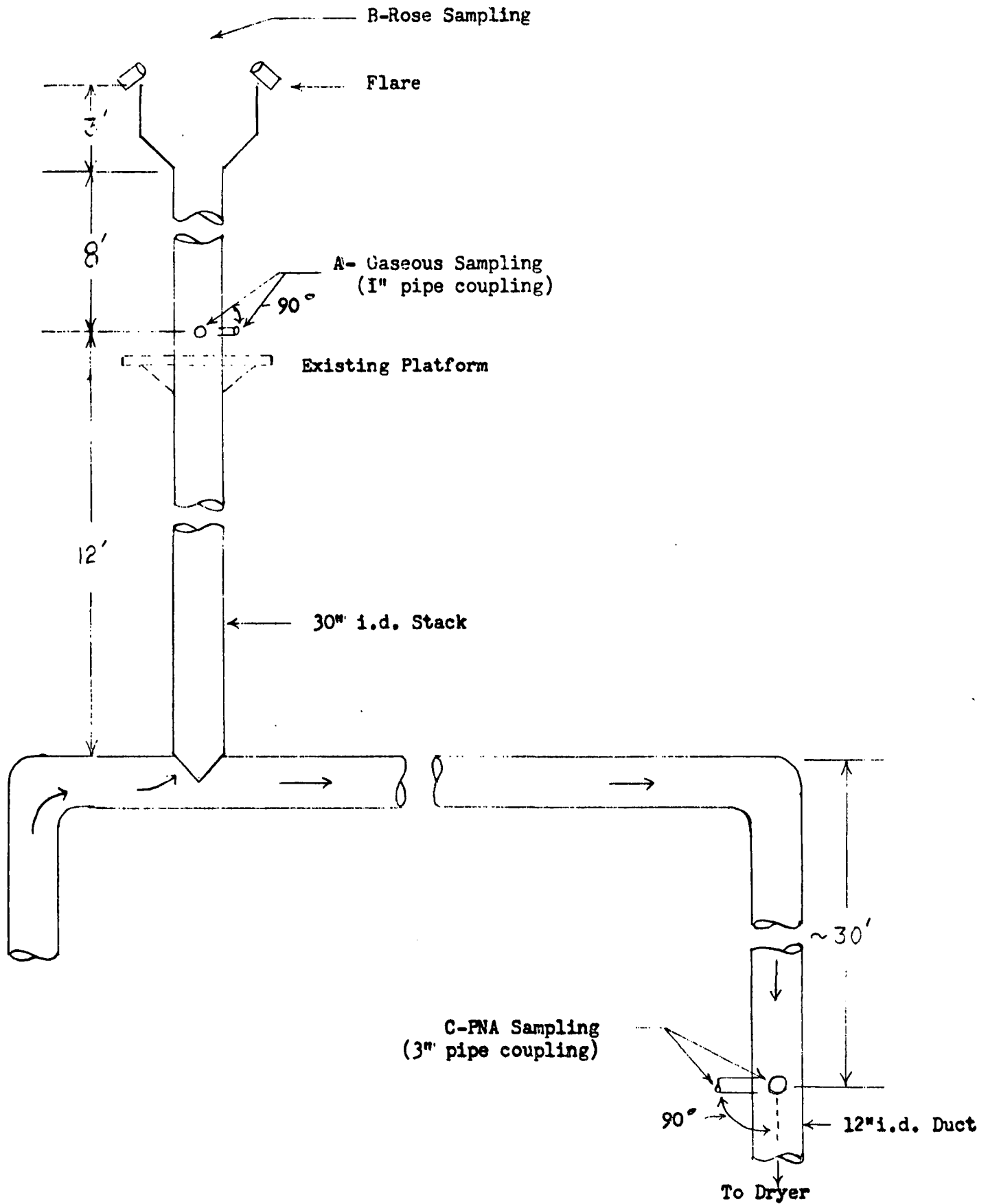


FIGURE 2. STACK GEOMETRY AND SAMPLING PORT LOCATIONS

off from the main stack (Point C) where a portion of the flue gas is fired as auxiliary fuel to heat the drying ovens. POM measurements were made on Unit No. 3 only.

Total Stack Flow

Gas velocity and stack temperature traverses were made in one direction only using Methods 1 and 2 procedures described in the Federal Register of December 23, 1971. A two direction traverse could not be made due to physical constraints of the sample platform. Total stack-gas flow was calculated by computing gas velocities at each traverse point and then determining the average gas velocity and flow rate. Table 2 gives the total stack-gas flow for each traverse.

Because of the number of samples to be collected, velocity profiles could not be measured simultaneously with collection of each sample. Hence, velocity profiles were determined prior to or after other sampling as can be noted from the sampling times shown in Tables 1 through 7.

Sampling and Analytical Procedures

Particulate and POM

Three particulate runs, to obtain samples for POM analysis, were made on Unit No. 3. Each run was conducted in parallel employing (1) EPA Method 5 (with a back-up "packed column" between the third and fourth impingers), and (2) a "packed column" sampling train. The sample probe for each train was located approximately 5 inches inside the duct, where velocity profiles showed the velocity head pressure to be fairly uniform at 1.1 in. H₂O. A 2-hour sampling period was employed for each run. Due to excessive pressure drop across the packed column isokinetic sampling was not maintained. It is believed that the divergence from isokinetic sampling was of little consequence since the particle size was quite small. Particulate samples were not used in establishing mass emission rates because the sampling location (Point C, Figure 2, or equivalent to upstream of the flare) was not suitable for obtaining particulate mass emission.

TABLE 2. TOTAL STACK GAS FLOW

Run No.	Unit No.	Date	Time	Total Stack dscm/min	Gas Flow, dscf/min
1	3	12/9/74	1600	327	11,549
2	3	12/11/74	0930	336	11,879
3	2	12/11/74	1300	429	15,164
4	2	12/12/74	1130	378	13,360

Mass loading particulate data, obtained from the filters used in the POM runs, are presented in Table 3. The two filters from Run No. 1 were inadvertently destroyed in the recovery process for POM analysis before weights could be obtained. Since all 3 POM runs were made in a similar manner (except for sampling rate), it is suggested that the mass particulate loading obtained on the filters from Run Nos. 2 and 5 are representative of particulate loading during Run No. 1, after the mass loadings obtained in Runs No. 2 and 5 are adjusted so that they conform to the sample volumes obtained in Run No. 1.

The POM analysis program provided for only one run (Run No. 1) to be analyzed. Because the POM data were not as significant as expected, it was mutually agreed that POM analysis of Run Nos. 2 and 3 would not be conducted at this time. However, these samples are being retained in POM storage until the final report is prepared for distribution.

Sample Recovery

The sample for POM analysis was recovered from the EPA Method 5 train as required by this method. To assure maximum recovery of POM, an additional methylene chloride rinse of the acetone rinsed impingers was made. In order to facilitate evaluation of the effectiveness of each portion of the Method 5 sampling train, each portion was separately analyzed as detailed below. The collected samples were recovered from the Battelle adsorbent sampling columns by continuous extraction with pentane for 24 hours.

<u>Sample Number</u>	<u>Sample</u>
1-1	Methylene chloride soxhlet extract (24 hours) of Method 5 filter together with acetone probe rinse.
1-2	Methylene chloride extract of the aqueous impinger contents and subsequent water rinse, together with the acetone rinse of the empty impingers.
1-3	Further rinse of the empty impingers with methylene chloride.
1-4	Pentane extract of adsorbent sampling column back-up to the Method 5 sampling train.
1-5	Pentane extract of the parallel adsorbent sampling column, together with the methylene chloride Soxhlet extract (24 hours) of its upstream filter, and the acetone rinse of the sampling probe.

TABLE 3. PARTICULATE DATA UNIT NO. 3

Run No. (2)	Mass (1) Loadings, gr.	Sample Volume DSCF	Stack Gas Volume DSCFM	Stack Moisture, Vol. Percent
1A	ND	66.79	1353	44.6
1B	ND	36.63	--	--
2A	0.2487	51.94	1356	44.4
2B	0.1761	35.26	--	--
5A	0.2410	53.29	1376	43.4
5B	0.1685	37.54	--	--

(1) Filter only

(2) Runs labeled "A" are using Method 5 sampling train,
Runs labeled "B" are using the packed column sampling train

An internal standard of 9-methyl anthracene was added to each of the above extracts, which were then reduced to a volume of about 2 mls by a rotary evaporator. A Rosen liquid chromatographic separation was then carried out on each of the extracts. The eluting fraction containing all POM species between anthracene and dibenzpyrenes, together with the eight NAS three and four star carcinogens, was collected and reduced to approximately 200 μ l using a Kuderna-Danish evaporator.

Analysis for POM Species

The above five samples were each quantitatively divided into two portions, one portion was quantitatively analyzed by gas chromatography-mass spectrometry (GC-MS) for the POM species present (except benz(a)pyrene). The other fraction was quantitatively analyzed by thin layer chromatography and spectrofluorimetry. GC-MS analysis was carried out using a Finnigan 1015 quadrupole mass spectrometer with a chemical ionization source. The reagent carrier gas used was methane. Gas chromatographic separation was carried out using a 12 foot 3% Dexil 300 column, programmed from 170 C to 350 C at 4 C min⁻¹. Data acquisition was carried out using a System Industries 150 Data Acquisition System with facilities for CRT display and print-out with XY plotter. The POM species present in each sample were detected by means of multiple ion overlay computer routines, which utilize prior knowledge of individual mass spectra and also make use of the methane ionization adduct ions at M+29 and M+41. Isomer assignments were made by means of relative GC retention times whenever possible.

Following the identification of the POM species present, quantification was carried out with reference to the internal standard using a

computer routine which permits integration of the appropriate mass spectral ions present in any computer reconstructed GC peak. We have previously demonstrated that this new integration routine has a reproducibility and accuracy of better than 7 percent over a very wide range of mass spectrometer conditions for the major species of interest in this program. Over the narrower range of conditions used in this work, the accuracy is rather better.

Benz(a)pyrene was separately quantified by the well-proven method involving spectrofluorimetric determination of the protonated species, following separation of the sample by thin layer chromatography (TLC). These experiments were conducted in dim amber lighting, to minimize sample decomposition. Samples were spotted in triplicate onto activated alumina TLC plates, and developed using a 5 percent solution of diethyl ether in hexane. (The TLC plates were previously pre-cleaned by 48 hours of Soxhlet extraction with an azeotropic mixture of chloroform and acetone; this Battelle developed procedure consistently reduces the plate "background" to less than 2 ng benz(a)pyrene equivalent.)

The developed samples were cut from the TLC plates with the aid of benz(a)pyrene markers on the sides of the plates, and the alumina was eluted with peroxide-free diethyl ether. This solvent was removed with a stream of nitrogen, the sample was immediately dissolved in 1.0 ml of concentrated sulfuric acid and transferred to a quartz cuvette for spectrofluorimetric quantitation in a Turner Model 210, using excitation of 4700 ± 25 A and emission of 5400 ± 100 A. The spectrofluorimeter was calibrated by means of approximately twenty determinations of 10 to 200 ng of pure benz(a)pyrene using an identical procedure to that employed for the unknown samples. The results of the POM quantification by GC-MS and spectrofluorimetry are tabulated below:

<u>POM Species</u>	<u>POM In Sample, ng</u>				
	<u>1-1</u>	<u>1-2</u>	<u>1-3</u>	<u>1-4</u>	<u>1-5</u>
Anthracene, phenanthrene	1750	8000	2360	10500	85800
Fluoranthene	9600	16200	4600	5650	10100
Pyrene	7700	54200	2080	21500	38700
Benz(a)anthracene, chrysene	-	1900	1400	400	1400
Benz(a)pyrene	<u>63</u>	<u>69</u>	<u>24</u>	<u>58</u>	<u>122</u>
Total POM (ng)	19,100	80,400	10,500	38,100	136,000

Apart from the small quantity of benz(a)pyrene, none other of the eight NAS three and four star carcinogens were detected. The absence of significant quantities of the POM species larger than four condensed benzene rings suggests very rapid quenching of the combustion effluents, which may be an inherent characteristic of carbon black manufacture.

The EPA Method 5 sampling train (110,000 ng) compared reasonably well with the Battelle adsorbent sampling column (136,000), but the non-quantitative nature of Method 5 is underlined by finding 38,100 ng of POM in the adsorbent sampling column used to back-up Method 5.

Hydrogen Sulfide (H₂S) by Method 11

Four H₂S runs were made on each unit (Unit Nos. 2 and 3), employing EPA Method 11, as outlined in the Federal Register of March 8, 1974. The results of the 8 runs are tabulated in Table 4. During the initial H₂S run, a yellow precipitate (CdS) was visually observed in the impingers. This is an indication that the capacity of the 3 absorbing impingers has been exceeded. To compensate for the relatively high concentration of H₂S in the stack gas, subsequent H₂S runs were made at a lower sampling rate. The analysis titration for H₂S was conducted at the sampling location in order to prevent loss of iodine from the sample. Table C-1 in the Appendix lists data and calculations associated with the H₂S determinations by Method 11.

In addition to EPA Method 11, H₂S and other sulfur compounds of interest (CS₂, COS, and SO₂) were analyzed by mass spectrometry (MS) at BCL. The analytical results for the MS runs are included in Tables 6 and 7. As was pointed out earlier, some disagreement is observed in the H₂S data acquired by the two methods. Visual observations at the sampling site gave some indication that the large concentrations of H₂S present in the stack gas were beyond the normal range for Method 11; hence, the values obtained by MS analysis are deemed to be more accurate. However, if the Method 11 sampling train is overloaded with H₂S, it would be expected to result in emission values that are too low. Conversely, the data in Table 1 show that the Method 11 train generally produced higher H₂S emission values than obtained by mass spectrometry. Possibly the iodine used in the Method 11 procedure is reacted with CS₂ so that the Method 11 procedure is not unique for H₂S.

Sulfur Dioxide (SO₂) by Method 6

Three SO₂ runs were made on each unit (Unit Nos. 2 and 3), employing EPA Method 6 as outlined in the Federal Register of December 23, 1971. One sample from each unit (Run Nos. 2 and 3) was voided due to a misaligned sampling probe on the first impinger which resulted in a leak in the sampling system. The results of the SO₂ runs are tabulated in Table 5. Sample analysis was conducted at the sampling location. Table C-2 in the Appendix lists data and calculations associated with the SO₂ determination by Method 6.

TABLE 4. SUMMARY OF HYDROGEN-SULFIDE DATA - EPA METHOD 11

Run No.	Unit No.	Date	Time	Sample Volume, Nm ³	Moisture, vol percent	H ₂ S, mg	H ₂ S mg/Nm ³	Emission	
								kg/hr	lb/hr
1A	3	12/10/74	1135-1150	0.0165	43	12.0	727	14.3	31.5
1B	3	12/10/74	1245-1300	0.0105	47	11.8	1123	22.0	48.5
2A	3	12/11/74	1040-1050	0.0051	45	9.9	1941	39.1	86.2
2B	3	12/11/74	1120-1130	0.0036	45	6.7	1861	37.5	82.7
3A	2	12/11/74	1640-1655	0.0056	48	8.8	1571	40.4	89.1
3B(a)	2	12/11/74	1748-1803	0.0080	47	6.7	838	21.6	47.6
4A(a)	2	12/12/74	0930-0940	0.0049	46	8.4	1714	38.9	85.8
4B(a)	2	12/12/74	1000-1010	0.0044	49	7.2	1636	37.1	81.8

(a) Stack flare out.

TABLE 5. SUMMARY OF SULFUR DIOXIDE DATA - EPA METHOD 6

Run No.	Unit No.	Date	Time	Sample Volume, Nm ³	Moisture, vol percent	SO ₂ , mg	SO ₂ , mg/Nm ³	Emission	
								kg/hr	lb/hr
1A	3	12/10/74	1135-1235	0.131	41	0.81	6.2	0.12	0.27
1B	3	12/10/74	1620-1720	0.128	41	4.15	32.4	0.64	1.41
2	3	12/11/74	1040-1140	0.125	2.6	0	Run voided ^(a)		
3	2	12/11/74	1645-1745	0.128	2.1	0	Run voided ^(a)		
4A ^(b)	2	12/12/74	0936-1041	0.120	43	21.89	182.4	4.14	9.13
4B ^(b)	2	12/12/74	1300-1400	0.135	43	32.83	243.2	5.52	12.17

(a) Run voided. Misaligned sample probe resulted in leak.

(b) Stack flare out.

Hydrocarbons and Reduced Sulfur Compounds

Three samples were obtained from each unit for combined gas chromatography (GC) and mass spectrometry (MS) analysis. The grab samples were taken in 3-liter volumetric glass bulbs and analyzed at BCL. The GC unit included a Packard, Series 800 with a flame ionization detector, and an Aerograph, Model 202 with a thermal conductivity detector. The MS used was a Consolidated Electrodynamics Corporation, Model 21-620.

The GC and MS are independent analyses; however, GC analyses are often used to compliment MS analyses when interference problems arise. For example, ethylene, ethane, carbon monoxide, and nitrogen all have the same nominal mass to charge ratio of 28 on the mass spectrometer. The GC provides accurate analysis for the above compounds which then may be used to make proper adjustments in the MS analyses. The MS provides a broad range of compounds not easily obtained by GC.

The hydrocarbons were analyzed using the GC instrument equipped with the flame ionization detector and a Porapak Q* column. The sulfur compounds, oxygen, nitrogen, hydrogen and argon are calculated from the mass spectra after proper adjustment for some hydrocarbons which might interfere.

Standard gas mixtures were used for calibration of the flame ionization detector. One standard mixture contains the saturated straight chain hydrocarbons and a second mixture contains the unsaturated straight chain hydrocarbons. Research grade gases are used to standardize the mass spectrometer data.

The analytical results for the GC-MS runs are compiled in Tables 6 and 7 for Units 3 and 2, respectively. Light hydrocarbon compounds (through C₄) are reported. The sulfur compounds of interest and additional components derived from the GC runs and MS runs using a mass-to-charge ratio through 100, are also reported in Tables 6 and 7.

* Trade name

TABLE 6. SUMMARY OF RESULTS - GAS CHROMATOGRAPHY, MASS SPECTROMETRY

Sample	Run No. 1 Date - 12/10/74 Time - 11:30			Run No. 2A Date - 12/11/74 Time - 9:15			Run No. 2B Date - 12/11/74 Time - 9:20		
	Emission			Emission			Emission		
	ppm	Kg/hr	lb/hr	ppm	Kg/hr	lb/hr	ppm	Kg/hr	lb/hr
H ₂ S	700	19.4	42.7	800	22.8	50.4	800	22.8	50.4
CS ₂	200	12.4	27.3	500	31.9	70.3	500	31.9	70.3
COS	90	4.4	9.6	60	2.9	6.6	70	3.5	7.7
SO ₂	< 50	< 2.6	< 5.7	< 50	< 2.6	< 5.7	< 50	< 2.6	< 5.7
CO ₂	38400	1376	3034	38600	1423	3137	39000	1438	3169
CO	118000	2691	5933	104000	2440	5379	115000	2698	5948
O ₂	4300	112.0	246.9	4700	126.0	277.7	2000	53.6	118.2
N ₂	644000	14692	32391	660000	15489	34148	645000	15135	33366
H ₂	168000	275.9	608	165000	278	614	171000	288.8	637
A	7400	241	531	7400	248	546	7300	244.1	538
CH ₄	6600	86.1	190	6700	89.9	198	7100	95.3	210.2
C ₂ H ₂	11800	250	551.5	11800	258	568	12000	261.6	576.7
C ₂ H ₄	340	7.8	17.2	358	8.4	18.6	343	8.0	17.8
C ₂ H ₆	< 5	< 0.1	< 0.2	< 5	< 0.1	< 0.2	< 5	< 0.1	< 0.2
C ₃ H ₆	6	0.2	0.5	13	0.5	1.0	7	0.2	0.5
C ₃ H ₈	29	1.0	2.2	33	1.2	2.7	29	1.0	2.3
C ₄ H ₁₀ (iso)	16	0.7	1.6	18	0.9	1.9	18	0.9	1.9
C ₄ H ₁₀ (n)	51	2.4	5.3	53	2.6	5.8	53	2.6	5.8

Note: Standard conditions = 70 F, 29.92 in. Hg.

TABLE 7. SUMMARY OF RESULTS - GAS CHROMATOGRAPHY, MASS SPECTROMETRY

Sample	Run No. 4A Date - 12/12/74 Time - 1415			Run No. 4B Date - 12/12/74 Time - 1420			Run No. 4C Date - 12/12/74 Time - 1425		
	Emission			Emission			Emission		
	ppm	Kg/hr	lb/hr	ppm	Kg/hr	lb/hr	ppm	Kg/hr	lb/hr
H ₂ S	600	19.3	42.4	400	12.9	28.3	700	22.4	49.6
CS ₂	400	28.7	63.3	600	43.0	94.8	500	35.8	79.1
COS	80	4.5	10.0	100	5.7	12.5	80	4.5	10.0
SO ₂	< 50	< 3.0	< 6.6	< 50	< 3.0	< 6.6	< 50	< 3.0	< 6.6
CO ₂	40600	1684	3711	41400	1717	3784	40500	1679	3702
CO	117000	3087	6806	117000	3087	6806	123000	3246	7156
O ₂	9300	280	618	8500	255.9	564.6	8600	256.9	572
N ₂	668000	17631	38870	664000	17530	38646	662000	17475	38524
H ₂	139000	264	582	143000	272.1	599	140000	266	586
A	7600	286	631	7700	289.4	639	7700	287.4	639
CH ₄	4400	66.5	146.5	4600	69.6	153.3	4600	69.6	153.3
C ₂ H ₂	12300	302	66.5	12700	311.7	686	12600	308.7	681
C ₂ H ₄	162	4.3	9.3	160	4.2	9.2	161	4.3	9.3
C ₂ H ₆	< 5	< 0.1	< 0.2	< 5	< 0.1	< 0.2	< 5	< 0.1	< 0.2
C ₃ H ₆	9	0.4	0.7	11	0.4	0.9	8	0.3	0.7
C ₃ H ₈	35	1.4	3.2	36	1.5	3.4	30	1.2	2.7
C ₄ H ₁₀ (iso)	14	0.7	1.7	11	0.6	1.3	14	0.7	1.7
C ₄ H ₁₀ (n)	43	2.3	5.2	64	3.6	7.8	63	3.5	7.6

Note: Standard conditions = 70 F, 29.92 in. Hg.

Carbon Monoxide (CO), Carbon Dioxide (CO₂) and Oxygen (O₂)

Measurement of CO was attempted by non-dispersive infrared technique, but levels were far in excess of the limit of the available instrument (6000 ppm). This problem was anticipated and CO determinations were made by two alternate methods, i.e., EPA Method 3 (Orsat) and gas chromatography of grab samples. Since carbon monoxide and nitrogen have the same nominal mass, a GC unit equipped with a thermal conductivity detector and a molecular sieve column was used to analyze the grab samples for carbon monoxide.

Five (Orsat) determinations of CO₂, O₂, and CO were made, using EPA Method 3 procedures--two from Unit No. 3 and three from Unit No. 2. The determinations made on Unit No. 3 were from duplicate samples, one analyzed by the Cabot Corporation and the other by BCL. A summary of the Orsat data is presented in Table 8.

Moisture

Moisture content of the gas stream was determined by EPA Method 4 procedures (measuring condensed water) during runs for determination of H₂S and SO₂. Moisture results are reported in Tables 4 and 5.

TABLE 8. SUMMARY OF ORSAT DATA

Run No.	Unit No.	Date	Time	Gas Analysis, percent		
				CO ₂	O ₂	CO
2A	3	12/11/74	3:00 p.m.	3.65	0.51	13.30
2B(a)	3	12/11/74	3:00 p.m.	2.20	0.30	12.80
4A	2	12/12/74	8:50 a.m.	2.91	0.90	12.45
4B	2	12/12/74	11:40 a.m.	3.10	0.50	13.80
4C	2	12/12/74	2:30 p.m.	3.30	0.90	13.50

(a) Analysis by Cabot.

Visible Emissions

Visual determination of the opacity of emissions from Unit Nos. 3 and 2 were obtained by two qualified observers. Two determinations were made on each unit by both observers. A summary of the visible emission data are compiled in Table 9. Observation records obtained by the observers are appended to this report.

Infrared Telespectrometer Measurements

The EPA infrared telespectrometer system, which bears the acronym ROSE (Remote Optical Sensing of Emissions), consists of a conventional quarter-meter grating monochromator, Hg:Ge and PbS detectors, associated electronic amplification and recording systems, and a specially designed telescopic optical system. This system allows the infrared emission spectra of warm (> 400 K) gaseous pollutants to be obtained from remote locations over the near infrared spectral regions of good atmospheric transmittance. For the flare measurements the ROSE system, which is housed in a mobile laboratory, viewed the flare at a slant range of 65 meters at an elevation angle of 30°. Data were obtained both with the flare on and off and also at various heights above the stack exit. The results of these measurements are described in Appendix B. The ROSE system is described in detail in EPA Report R2-72-052.

Recommendations on Sampling Procedures

The following comments are based upon observations made during the stack-emission-sampling program at the Cabot Corporation carbon-black plant in Waverly, West Virginia.

H₂S - EPA Method 11

It appears that EPA Method 11 is not completely applicable (at least without modification) in determining H₂S emissions from stationary sources where high concentrations of H₂S and moisture are prevalent. The method is based upon procedures developed by the petroleum industry

TABLE 9. SUMMARY OF VISIBLE EMISSIONS

Run No.	Stack No.	Date	Time	Opacity, percent					
				Minimum		Maximum		Average	
				Ob.A	Ob.B	Ob.A	Ob.B	Ob.A	Ob.B
2A	3	12/11/74	12:48-13:48	5	5	15	15	9.6	9.9
2B	3	12/11/74	15:20-16:20	5	5	15	15	7.4	8.3
3A	2	12/11/74	11:02-12:02	5	5	40	40	15.9	18.6
3B	2	12/11/74	14:09-15:09	5	5	30	40	9.7	11.0

and natural gas producers-API Method 772-54. It was designed for use in gas streams where relatively low concentrations of H_2S and moisture are encountered. The possibility of interference of other reduced sulfur compounds should be investigated.

There were indications that the high concentration of H_2S (727-1941 mg) encountered at the Waverly plant exceeded the capacity of the three absorbing impingers in the sampling train. This was visually observed by the yellow color (CdS) in the impingers, which even occurred at sampling rates considerably slower than those recommended in the Method.

There are several practical modifications which can be made to Method 11 where relatively high concentrations of H_2S (> 100 ppm) are anticipated. One modification, requiring very little readjustment of the procedure, would be to increase the strength of the H_2S absorbant solution [$Cd(OH)_2$] and the iodine-thiosulfate titrating reagent.

When high moisture content (40 to 50 percent) is encountered in the stack gas, as was found at the Cabot carbon-black plant in Waverly, an additional empty impinger in the number two position (immediately behind the 3 percent H_2O_2 impinger) would help prevent splashover of condensed moisture and acid mist from the first impinger into the H_2S absorbing impingers.

SO₂ - EPA Method 6

The aforementioned moisture problem may also seriously effect SO_2 determinations employing EPA Method 6. An empty impinger located in the number two position of this train would also help prevent splashover of acid mist and sulfur trioxide.