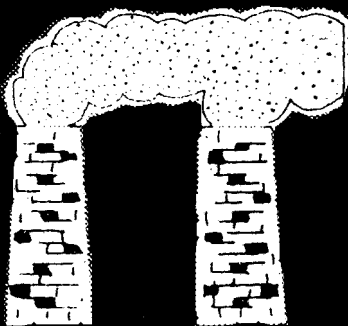
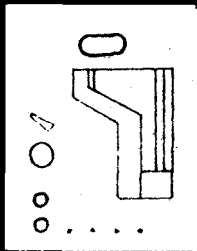
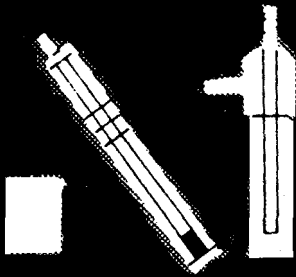


AIR POLLUTION EMISSION TEST

CHAMPION INTERNATIONAL

Pasadena, Texas

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



SOURCE TEST REPORT

EPA No.: 72-PC-11.

Particulate and Gaseous
Emissions From
A Kraft Pulp Mill

U. S. PLYWOOD - CHAMPION PAPERS
Pasadena, Texas

EPA Contract No.: 68-02-0232
Task No.: 7

Environmental Engineering, Inc.
2324 Southwest 34th Street
Gainesville, Florida 32601

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I. INTRODUCTION

In accordance with Section 111 of the Clean Air Act as amended of 1970, the Environmental Protection Agency is charged with the establishment of performance standards for new stationary sources which may contribute significantly to air pollution. These standards are based upon the best air pollution control technology that has been demonstrated.

This report presents the results of an extensive source testing program conducted at Champion Paper Company, Pasadena, Texas, June 3-9, 1972, to obtain data for a partial basis in consideration of new source performance standards in the kraft pulping industry.

Stack emissions were measured from the chemical recovery boiler for particulate, sulfur dioxide, reduced sulfur compounds, oxides of nitrogen, carbon dioxide, carbon monoxide, and oxygen. Emissions from the first and second stages (individually vented) of the black liquor oxidation system were also measured for sulfur dioxide and reduced sulfur. The recovery boiler utilizes a cascade direct contact evaporator and strong black liquor oxidation and exit gases are controlled with an electrostatic precipitator.

Reduced sulfur compounds were measured by flame photometric gas chromatography and coulometric titration. Carbon monoxide and carbon dioxide were measured with infrared analyzers and oxygen was monitored with a paramagnetic oxygen analyzer. All other stack emissions were measured with EPA reference methods.

II. SUMMARY AND DISCUSSION OF RESULTS

Table 1 summarizes results of gaseous sulfur determinations utilizing both flame photometric and coulometric detection systems. All summary results are reported in terms of TRS as H_2S . TRS is defined as hydrogen sulfide plus methyl mercaptan plus dimethyl sulfide plus dimethyl disulfide; all compounds are reported as hydrogen sulfide. It should also be noted that dimethyl disulfide (RSSR) concentrations, determined with the chromatographic system, are assumed to yield twice those concentrations when considered as hydrogen sulfide. Complete gaseous sulfur data is contained in Appendix A.

Results from the particulate emission tests on the recovery furnace are shown in Table 2. Emission rates were calculated on the basis of the moisture content determined from a separate moisture test instead of the condensed moisture in the impingers. The reason for this is that the evaporation rate of the isopropanol in the impingers was found to be excessive based upon previous tests.

The third and fourth impingers, which contained 3% hydrogen peroxide, were analyzed for sulfur dioxide by using barium perchlorate titrations. The data are also included in Table 2.

Complete particulate and sulfur dioxide data are contained in Appendix B.

Daily mean concentrations for oxygen, carbon dioxide, and carbon monoxide are presented in Table 3. The results are reported on a dry

gas basis. Complete results of the gas concentrations at 15-minute intervals are included in Appendix C.

The results from the nitrogen oxide emission testing are summarized in Table 4. Complete NO_x data are included in Appendix B.

Table 1

TRS DAILY AVERAGES

(Coulometric and Flame Photometric Detection)

U. S. PLYWOOD - CHAMPION PAPERS
Pasadena, Texas

Date	Source	Flame Photometric Detection			Coulometric Detection		
		ppm (1)	lbs/hr	lbs/ADTP	ppm	lbs/hr	lbs/ADTP
6-3-72	PPT Outlet	2.02 (2)	1.54		4.1	3.13	
6-4-72	PPT Outlet	1.41 (3)	1.06		2.9	2.19	
6-5-72	PPT Outlet	1.40	1.06		2.7	2.04	
6-6-72	PPT Outlet	1.54	1.16		2.5	1.88	
6-7-72	PPT Outlet	0.77	0.58		2.9	2.19	
6-8-72	PPT Outlet	1.58	1.20		3.1	2.35	
6-9-72	1st Stage BLO (5)	38.90	1.21		48.8	1.52	
	2nd Stage BLO	23.25	0.62		6.8	0.18	

(1) Parts per million by volume - Dry Gas Basis

(2) H₂S only

(3) RSR & RSSR

(4) H₂S & RSH

(5) BLO - Black Liquor Oxidation

TABLE 2
PARTICULATE AND SULFUR DIOXIDE EMISSIONS

	<u>Run #1</u>	<u>Run #2</u>	<u>Run #3</u>
Date	6/3/72	6/5/72	6/6/72
Time Began	12:45	9:25	9:52
Time End	18:23	13:05	13:32
Barometric Pressure, In. Hg Absolute	30	30	30
Meter Orifice Pressure Drop, In. H ₂ O	0.14	0.14	0.09
Vol. Dry Gas @ Meter Conditions, ft ³	42.431	42.530	45.294
Average Gas Meter Temperature, °F.	86	87	89
Vol. Dry Gas @ S.T.P.* , ft ³	41.312	41.333	43.853
Stack Gas Moisture, % Volume	25.5	25.3	21.9
% CO ₂	10.4	10.7	11.8
% O ₂	10.7	11.4	10.1
% CO	0	0	0
% N ₂	78.9	77.9	78.1
Average Stack Gas Temperature, °F.	314.2	304.2	302.6
Stack Pressure, In. Hg Absolute	30.07	30.07	30.07
Stack Gas Velocity @ Stack Cond., fpm	4633	4683.6	4554.1
Stack Gas Flow Rate @ S.T.P.* , scfm	141512	145321	148042
Net Time of Test, min.	180	200	200
Percent Isokinetic	113.4	99.4	103.5
Particulate Concentrations, grains/scf			
Front half and Filter	0.085	0.096	0.092
Total	0.184	0.199	0.197
Particulate Emissions, lbs/hr			
Front half and Filter	103.32	110.07	116.51
Total	223.04	248.18	250.03
Particulate Emissions, lbs/ton ¹			
Front half and Filter	4.13	4.40	4.66
Total	8.92	9.93	10.00
SO ₂ Emissions, lbs/hr	14.77	63.82	Neg.

* Dry, 70°F., 29.92 in. Hg

¹ Based upon 600 tons ADP/day

Table 3

Carbon Dioxide, Oxygen, and Carbon Monoxide Concentrations

Date	Daily Averages		
	CO (ppm)	CO ₂ %	O ₂ %
6/3/72	153	10.4	10.7
6/4/72	93	8.2	11.4
6/5/72	84	10.7	11.4
6/6/72	95	11.8	10.1
6/7/72	102	12.9	10.1
6/8/72	51	11.1	9.9

Table 4

Nitrogen Oxide Concentrations No. 6 Recovery Furnace Outlet

Date	Time	NO _x , ppm
6/3/72	1605	19.3
	1830	19.8
6/5/72	1400	19.8
	1630	24.2
	1700	17.9
6/6/72	1440	20.2
	1535	34.3
	1600	34.5

III. PROCESS DESCRIPTION AND OPERATION

The Champion International Plant at Pasadena, Texas is a complete mill, producing 600 tons of fine paper and newsprint per day from its own bleached kraft pulp and groundwood. The EPA test program at this mill was limited to two facilities; the black liquor oxidation system, and the recovery furnace system. These systems are a small but important part of the plant complex, and are part of the process for recovering spent cooking chemicals from the kraft pulping operation. Diagrams of both systems are shown in Figure 1.

Process Description

A. General

The mill produces kraft pulp by cooking wood chips in white liquor, a water solution of sodium hydroxide and sodium sulfide. The spent cooking solution, called black liquor, is treated to regenerate cooking solution. During regeneration, the black liquor is concentrated in evaporators and then burned in a recovery furnace. At the furnace bottom, inorganic chemicals are recovered as a sodium carbonate-sodium sulfide smelt. The molten smelt is tapped off and dissolved in water. The resulting mixture, called green liquor, is drawn from the dissolving tank and treated with lime to complete the regeneration of cooking solution.

Heat released in the recovery furnace from combustion of the black liquor is used to generate process steam and to complete the evaporation of additional black liquor. The recovery furnace, sometimes called a

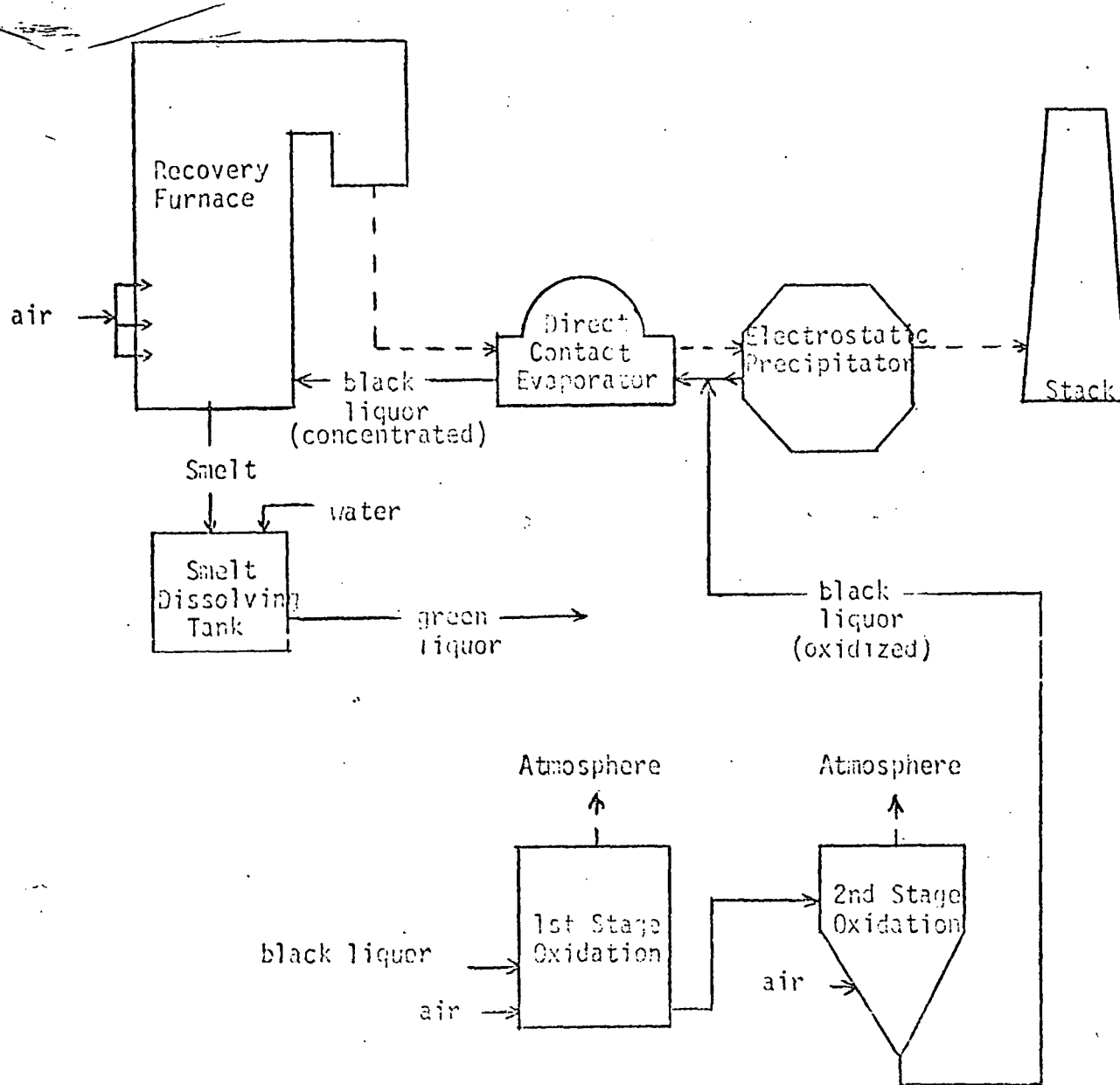


Figure 1. Flow Diagram of Recovery Furnace and Black Liquor Oxidation system.

recovery boiler, employs water walls and boiler tubes to absorb part of the available heat. Combustion gases leave the furnace at about 700°F and go to a direct contact evaporator; black liquor, fed counter-currently to this unit, contacts the hot gases directly and is evaporated to a solids content of about 60 percent. The concentrated liquor is sprayed into the furnace; combustion gases leaving the direct contact evaporator are cleaned in an electrostatic precipitator and then vented to the atmosphere through a tall stack.

Chemical reactions between the combustion gases and black liquor in the direct contact evaporator can generate hydrogen sulfide. To inhibit these reactions the black liquor is first sparged with air in a two stage oxidation system. Oxidation converts sulfide in the liquor to thiosulfate and effectively reduces subsequent hydrogen sulfide formation.

B. Recovery Furnace System

The test unit was installed in 1958 and designated the #6 recovery furnace. This furnace was designed by Babcock and Wilcox for a heat input of 575 million BTU per hour, equivalent to a pulp production rate of 650 tons per day. Associated with this furnace is a cascade direct contact evaporator.

A portion of the product steam is used to blow soot from the boiler tubes. Tubes are cleaned continuously, one section at a time.

C. Oxidation System

The oxidation system was designed by Champion to oxidize strong black liquor by sparging with air in two sequential stages. The first stage was installed in 1951 and the second stage in 1967. In each stage, air is blown through the black liquor and vented through a cyclone to the atmosphere. Number 2 heating oil is pumped to the second stage at about 15 gallons per hour to inhibit foaming, and each stage has a foam breaker. Black liquor from the cyclones and foam breakers are recycled. The oxidation system serves two recovery furnaces with a total equivalent pulp production of 900 tons per day.

D. Electrostatic Precipitator

The precipitator was designed for a collection efficiency of 98 percent and installed by the Koppers Company in 1958. Inlet gas is divided into three parallel chambers, and each chamber has three fields. The inlet fields of chambers 1 and 2 are coupled electrically; the center fields of chambers 2 and 3 are also coupled. Accordingly, the precipitator has seven separately controlled sections.

Rappers operate every 2 1/2 minutes; during each cycle the inlet sections rap for 5 seconds, followed by the center sections for 10 seconds, and the outlet sections for 15 seconds. Salt cake drops to the hoppers and is recycled to the recovery furnace by circulating black liquor.

Process Operation

During testing, records were kept of process variables for the recovery furnace, electrostatic precipitator, and the black liquor

oxidation system. Wherever process monitors were available, operating conditions that affect emission rates were recorded. The raw process data sheets and a key explaining the entries are included in the Appendix D.

A. Recovery Furnace

The process records, as well as statements by the operators, indicate that during the tests the recovery furnace was operated normally. The observed ranges of major operating variables are given in Table 5; where information is available from the company, the design and normal values are also shown. As seen from the table, black liquor feed rate, solids content, and steam temperature, pressure, and production rate, were all within a few percent of normal; reduction ratio was greater than 95 percent, as proper. (Reduction ratio, determined from green liquor samples, is the concentration of sodium sulfide divided by the sum of sodium sulfide and sodium carbonate concentrations.) These records show that the furnace received a normal charge and performed its major functions (production of smelt and steam) in a normal way during the tests.

Many operating parameters (such as distribution of furnace combustion air, manner of spraying feed liquor, etc.) affect furnace emissions. Those that could be monitored were recorded. There is no indication from the records or from operators' statements that unusual practices were followed.

The sodium sulfide concentration in black liquor fed to the direct contact evaporator is a process variable of special interest, because of its strong influence on the generation of hydrogen sulfide. Sulfide levels are determined routinely by the Company and were made available for the

test period. As shown in Table 6, sulfide levels were frequently undetectable; the highest levels (June 5 and 6) caused no measurable increases in hydrogen sulfide emissions.

B. Black Liquor Oxidation System

A limited amount of process data was obtained June 9 during tests on the oxidation system. Readings of the available process monitors were recorded on data sheets included in the appendix. These data are summarized in Table 7.

As far as known from the process data and statements by the operators, the oxidation system was operated normally during the test.

C. Electrostatic Precipitator

Precipitator operation was monitored during all the furnace tests. Primary current, secondary current, and secondary voltage in each of the seven control sections were recorded hourly. The raw data sheets are included in the appendix. These data are summarized in Table 8; information supplied by Champion International on design and normal operating conditions is included where available.

During most of the particulate sampling the precipitator was operated normally. The major exception occurred in the first run; during the last hour of sampling, the primary current in one control section dropped from about 78 to 46 amperes. (Particulate emissions, however, were lowest for this run.) The second run was postponed a day until the precipitator was repaired. When the faulty section was cleaned out and several damaged collector plates were welded into place, normal current was restored.

Table 5. SUMMARY OF THE RECOVERY FURNACE PROCESS DATA

Operating Condition	Units	Design ^(a)	Normal	During Test 6/3-8/72	Item No. on Data Sheets
Black Liquor Feed Rate	GPM	200 ^(b)	208	214-223	10
Black Liquor Solids Content	Wt. %	67	65	64.2-66.5	14
Steam Production ^(c)	10 ³ lb/hr	299	225 ^(d)	200 - 255	1
Steam Temperature	°F	750	700	670 - 750	4
Steam Pressure	psig	375	330	321 - 357	5
Reduction Ratio ^(e)	%			95.7 - 97.1	

(a) Information supplied by Champion International.

(b) Calculated by Champion International from design heat input using current operating parameters.

(c) Net production, not including steam used for soot blowing in the recovery furnace.

(d) Original design did not contemplate current rate of saturated steam usage for soot blowing.

(e) $(100)(\text{Na}_2\text{S})/(\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4)$

Table 6. SODIUM SULFIDE CONCENTRATIONS IN BLACK LIQUOR FED
TO THE DIRECT CONTACT EVAPORATOR

Date 1972	Time 24 hour	Sodium Sulfide ^(a) grams/liter
3	1330	0.0
4	0700	0.117
4	1430	0.0
5	0730	0.390
5	1500	0.0
6	0745	0.265
6	1530	0.156
7	0645	0.195
7	0710	0.0
8	1315	0.0
9	0640	0.0

(a) Determined by Champion International by potentiometric titration.

Table 7. SUMMARY OF PROCESS DATA FOR THE BLACK LIQUOR OXIDATION SYSTEM

Stage 1

Operating Condition	Units	Design	Normal	During Test (6/9/72)
Black Liquor Feed Rate	GPM	535	542	350 - 500
Air Feed Rate	SCFH	6000		not measured
Air Feed Pump Pressure	psig	6		6 1/4 - 6 1/2

Stage 2

Operating Condition	Units	Design	Normal	During Test (6/9/72)
Air Feed Rate	SCFH	5000		not measured
Air Feed Pump Pressure	psig	6		6 3/4

NOTE: Stage 2 liquor feed rate is not measured; it is slightly less than stage 1 because of evaporative water losses in stage 1.

Table 8. SUMMARY OF PROCESS DATA FOR THE ELECTROSTATIC PRECIPITATOR

Operating Condition	Units	Design	Normal	During Test 6/3,5,6/72
Gas Volume	10^3 ACFM	281	265	273-281
Gas Temperature	°F	325-350	325	303-314
Inlet Loading	gr/SDCF	2.5-6.0	4.0	---
Outlet Loading	gr/SDCF	0.05 ^(a)	0.10 ^(a)	0.085-0.096 ^(b)
Efficiency	%	98	97.5	---
Primary Current	amps	90	85-95	46 - 96 ^(c)
Primary Voltage	volts	440		310 - 400
Secondary Voltage	10^3 volts	65	45-60	
Secondary Current				325 - 490

(a) Texas Air Control Board method; similar to EPA Method 5.

(b) EPA Method 5; front half only.

(c) Primary current in one control section was low for about 30 minutes;
minimum current at all other times during particulate testing was 70 amps.

IV. LOCATION OF SAMPLING POINTS

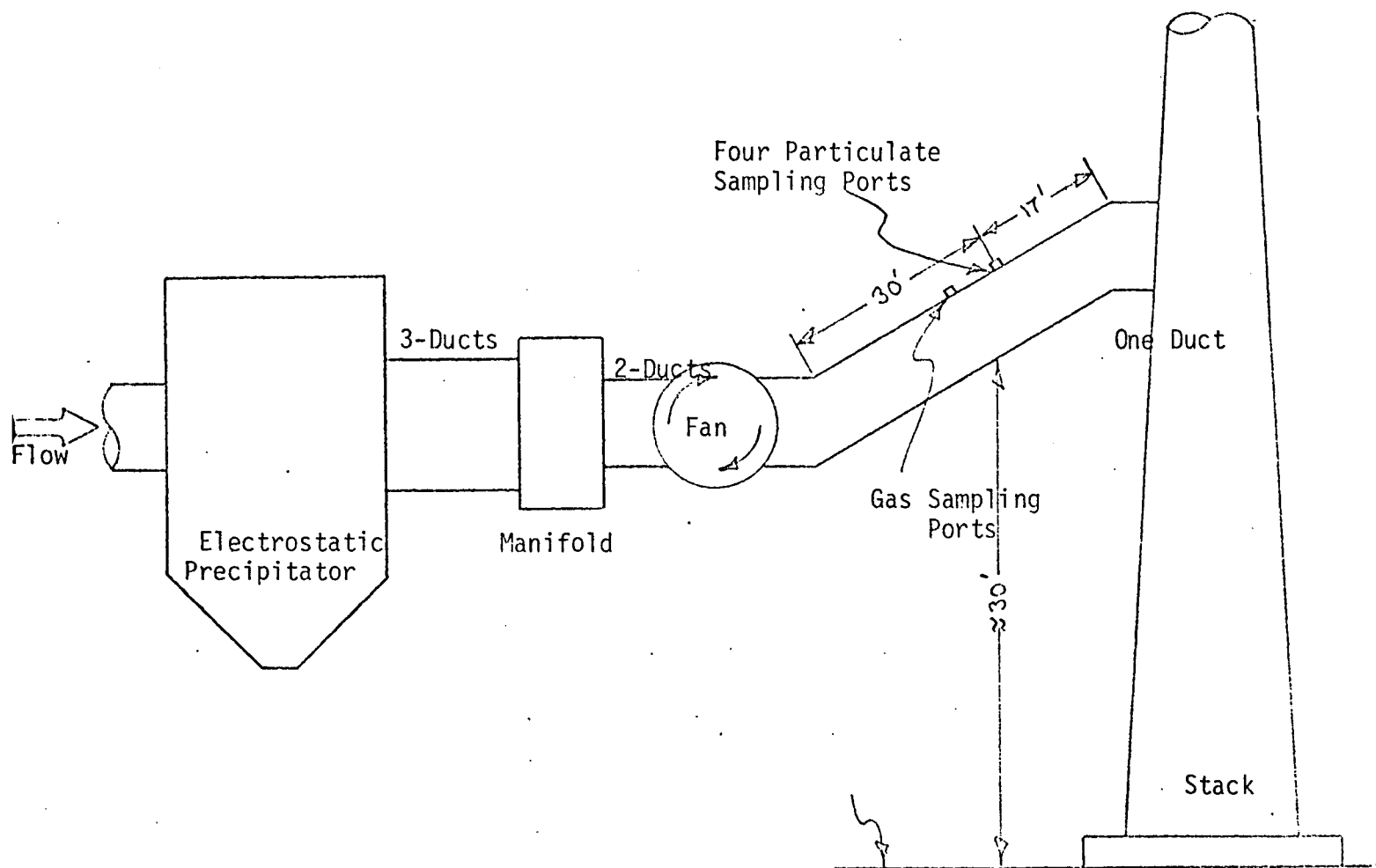
The outlet stack from the electrostatic precipitator on the No. 6 recovery furnace was sampled at the rectangular duct entering into the vertical stack, as shown in Figures 2 and 3.

The traverse points sampled in each of the four ports are as follows:

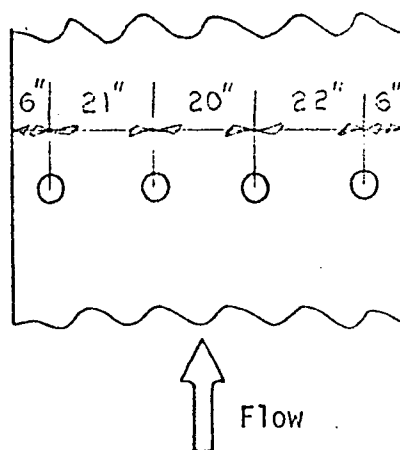
<u>Sample Point No.</u>	<u>Distance From Inside Wall, In.</u>
1	5 3/4
2	17 1/4
3	28 3/4
4	40 1/4
5	51 3/4
6	63 1/4
7	74 3/4
8	86 1/4
9	97 3/4
10	109 1/4

NOTE: The traverse points were utilized for determination of particulates, gas volumes, moisture and other necessary stack gas parameters.

The gaseous constituents were extracted from the source gas stream based upon the assumption that the gases were homogeneously mixed. Therefore, gaseous sulfurs, nitrogen oxides, carbon dioxide, oxygen and carbon monoxide were sampled from relatively fixed points in the gas handling system.



SIDE VIEW OF NO. 6 RECOVERY
FURNACE GAS OUTLET
Figure 2



TOP VIEW OF PARTICULATE
SAMPLING PORTS
Figure 3

V. SAMPLING AND ANALYTICAL PROCEDURES

Chromatographic Sampling System

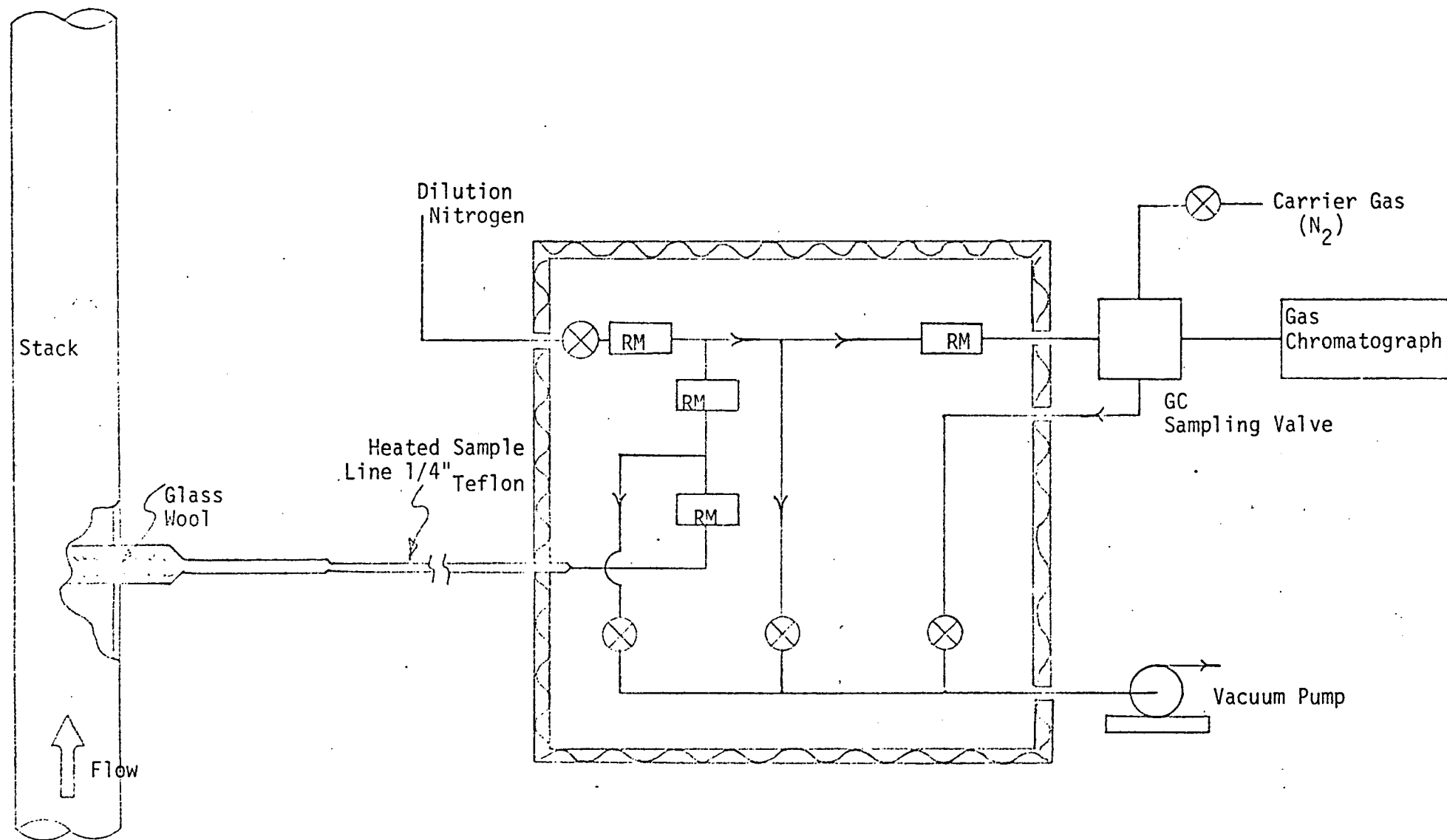
Figure 4 illustrates the system which was employed in conveying the gases from the source to the sensing equipment. The stainless steel probe and Teflon sampling line were maintained at temperatures exceeding the dew point of the source gases. The sampling line consisted of an insulated, electrically heated 1/4-inch Teflon tube. The sample gases were transmitted to the heated dilution box where they were split into two separate streams. One stream was conveyed to the vacuum source and wasted to minimize lag time in the sampling line. The remainder of the flow was diluted with nitrogen by an amount sufficient to lower the dew point of the gases below ambient temperature. A portion of this diluted sample was injected into the chromatograph through the Gas/Liquid Chromatograph (GLC) sampling valve. The remainder of the diluted gas was wasted through the vacuum source.

Chromatographic Analysis

Gaseous sulfur concentrations were determined with a Tracor Model 250 Gas/Liquid Chromatograph. This unit is equipped with a flame photometric detector which is specifically for sulfur compounds. Two analytical columns were utilized in the separation and analysis of the gaseous sulfur compounds. One was a 36-foot by 1/8-inch OD Teflon column packed with polyphenyl ether liquid phase on a solid support of granular Teflon with stripper column. The second column, constructed of identical materials, was 8 feet long. Both columns were operated at 50°C.

The 36-foot column was utilized for analyzing hydrogen sulfide, sulfur dioxide, and methyl mercaptan while the 8-foot column facilitated the analysis of dimethyl sulfide and dimethyl disulfide.

The chromatograph was calibrated for hydrogen sulfide, sulfur dioxide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide, using the spinning syringe technique.



GC GAS SAMPLING SYSTEM
Figure 4

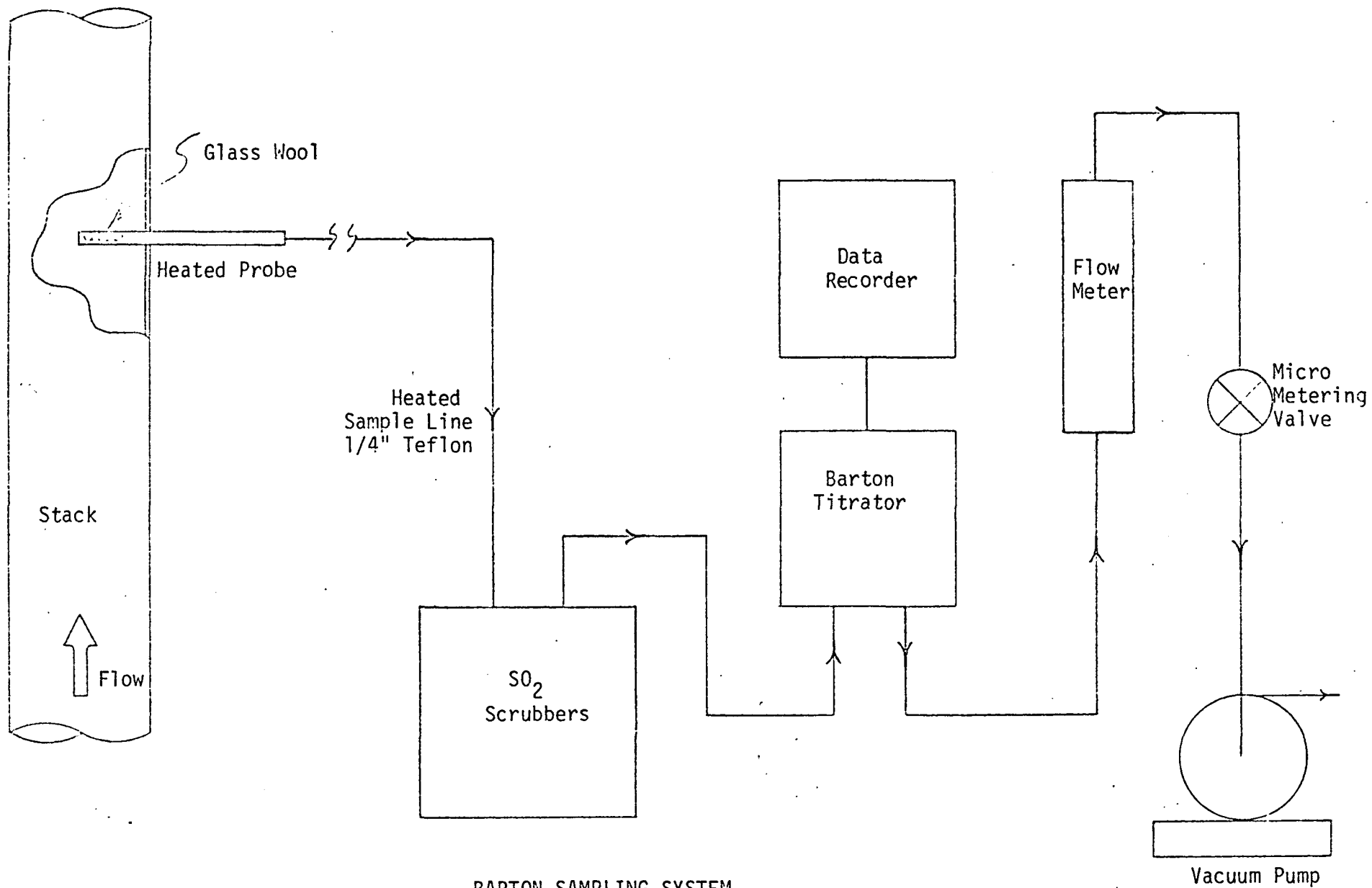
RM: Rotameter
⊗: Metering Valve

Coulometric Detector (Barton Titrator)

Figure 5 illustrates the system which was employed in conveying the gases from the source to the Barton Titrator. The stainless steel probe and Teflon sampling line were maintained at temperatures exceeding the dew point of the stack gases. The sampling line was the same as the sampling line used with the GLC. The sample gases were transmitted to the Barton Titrator by a vacuum source.

Barton Titrator

Total reduced sulfur (TRS) concentrations were analyzed using a Barton Titrator, Model 400. Furnace gases were scrubbed through a 3% solution of potassium acid phthalate (KHP) which removes sulfur dioxide and a large fraction of water vapor from the sample gases. The sample gas was then introduced to a coulometric titration cell which utilizes hydrobromic acid (HBr) as an electrolyte. The electrolytic cell generates bromine from the HBr electrolyte which reacts with the sulfur compounds entering the titration cell. The quantity of current required to generate the excess bromine, to consume the sulfur compound, is proportional to the gaseous sulfur concentrations introduced. The current required to operate the titration cell is sensed and transmitted to a recorder where a continuous readout is accomplished. The recorded output is converted to TRS concentrations, as H_2S from calibration data generated with the "spinning syringe" technique.



BARTON SAMPLING SYSTEM
Figure 5

Sampling Procedure for Particulate Emissions

Prior to performing the actual particulate emission tests, certain preliminary stack parameters had to be determined for the stack gases. This preliminary data included the average stack gas temperature, velocity head, moisture content, stack dimensions, and number of sampling points.

The stack gas temperature was determined by using bimetallic thermometers and a pyrometer.

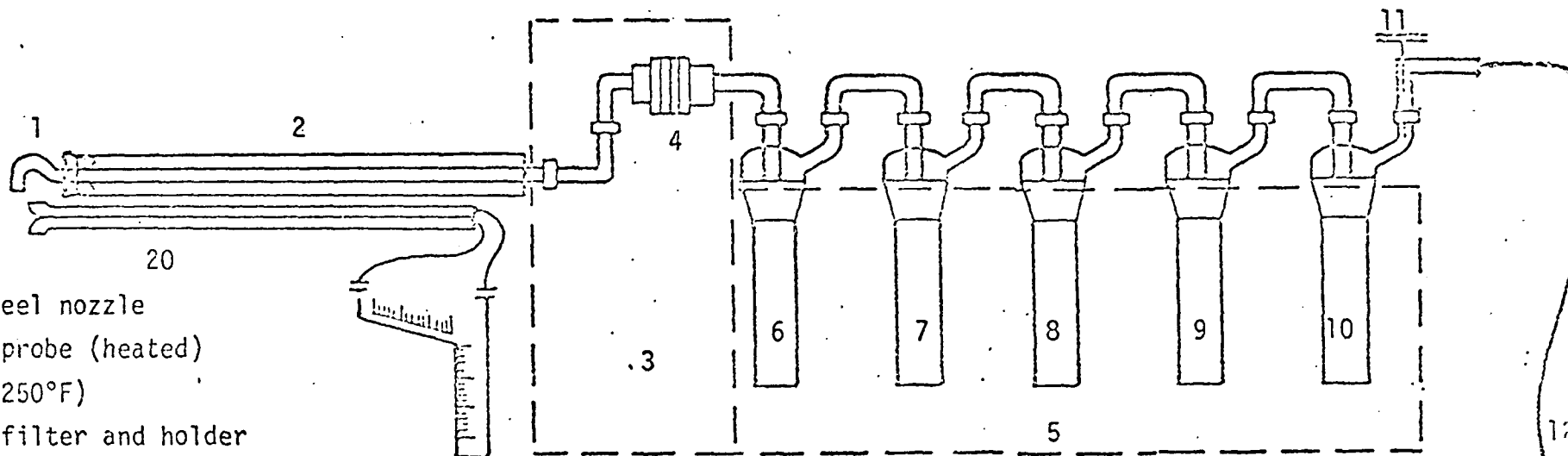
The approximate stack gas moisture content selected for setting the nomograph was based upon previous tests made on the same boiler. The final moisture content used in calculating the stack emissions from the recovery furnace was based upon the amount of condensate collected in the impingers and the silica gel from a separate moisture test.

The sampling points selected and the respective stack gas velocities were determined by using Methods No. 1 and 2 of the Federal Register (Vol. 36, No. 247, December 23, 1971). Velocity head measurements were made by using a calibrated S-type pitot tube with an inclined manometer.

The sampling train configuration used during the tests consisted of the following: a stainless steel nozzle; a heated glass-lined probe; a heated glass-fiber filter; two Greenburg-Smith impingers with tips, each containing 100 ml of 80% isopropanol; two Greenburg-Smith impingers without tips, each containing 100 ml of 3% hydrogen peroxide; one Greenburg-Smith impinger without a tip, containing about 200 grams of silica gel; a flexible sample line; an air-tight vacuum pump; a

dry-test meter; and finally a calibrated orifice with an inclined manometer (see Figure 6). Velocity head measurements were conducted simultaneously with the sampling at each point so that each point could be sampled isokinetically.

The impinger portion of the sampling train was iced down to collect the condensables, and to determine the actual stack gas moisture.



1. Stainless steel nozzle
2. Glass-lined probe (heated)
3. Heated box (250°F)
4. Glass-fiber filter and holder
5. Ice bath
6. Impinger with Tip, 100 ml of 80% Isopropanol
7. Impinger with Tip, 100 ml of 80% Isopropanol
8. Impinger without Tip, 100 ml of 3% H_2O_2
9. Impinger without Tip, 100 ml of 3% H_2O_2
10. Impinger with 200 grams of Silica Gel
11. Thermometer
12. Flexible sample line
13. Vacuum gauge
14. Coarse valve
15. Fine valve
16. Vacuum pump
17. Drg-test meter
18. Calibrated crifice
19. Inclined manometer
20. S-type pitot tube

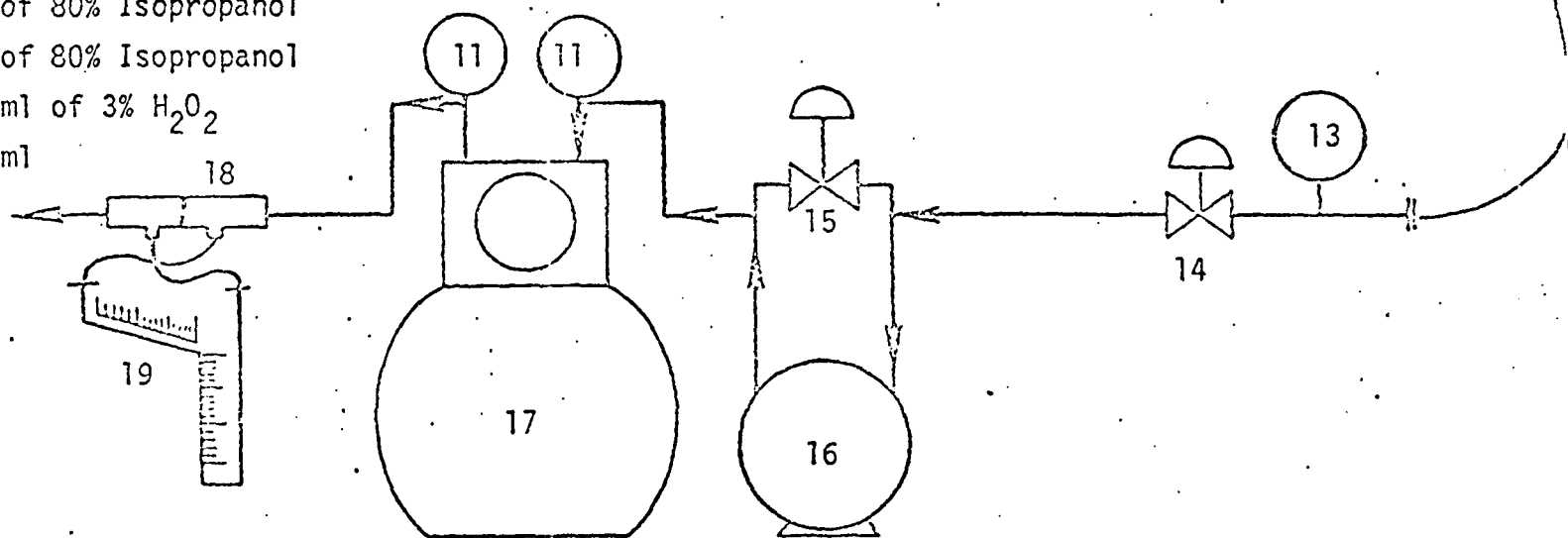


FIGURE 6
PARTICULATE AND SO_2 TRAIN

Sample Recovery and Analyses of Particulates

Sample recovery from the particulate train was accomplished by separating train components into the following containers:

Container No. 1 - The previously weighed glass-fiber filter was placed into this container, then sealed and labeled.

Container No. 2 - All portions of the train from the nozzle through the front half of the filter holder were rinsed with acetone and the contents placed into a glass container, then sealed and labeled.

Container No. 3 - The volume of liquid from the first and second impingers was measured and the contents placed into a glass container. Also, all sample-exposed surfaces between the filter and third impinger were rinsed with 80% isopropanol and placed into this container, then sealed and labeled.

Container No. 4 - The volume of liquid from the third and fourth impingers was measured and the contents placed into separate glass containers. All glassware between the second and fifth impingers was then rinsed with deionized, distilled water and then added to each respective container. The liquid samples were then sealed and labeled. Only one sample container was used for both impingers used in the smelt dissolving tank sampling.

Container No. 5 - The previously weighed silica gel was removed from the fifth impinger and placed into the original polyethylene jar and sealed.

The samples recovered were analyzed as follows:

Container No. 1 - The filter and all loose material in the sealed petri dish were transferred to a tare glass weighing dish, desiccated, and dried to a constant weight.

Container No. 2 - The acetone washings were transferred to a tared beaker and evaporated to dryness at ambient temperature and pressure. It was desiccated and dried to a constant weight.

Container No. 3 - The contents were transferred to a tared beaker, and then evaporated at 212°F. The residue was desiccated and dried to a constant weight.

Container No. 4 - The liquid contents were shaken, and then a 25 ml aliquot of each container was pipetted into separate 250 ml Erlenmeyer flasks. One hundred ml of isopropanol, plus two to four drops of thorin indicator was added to each sample. The samples were titrated with barium perchlorate to a pink end point. Another duplicate sample and blank was titrated in the same manner as the first sample. Samples were analyzed at the plant site.

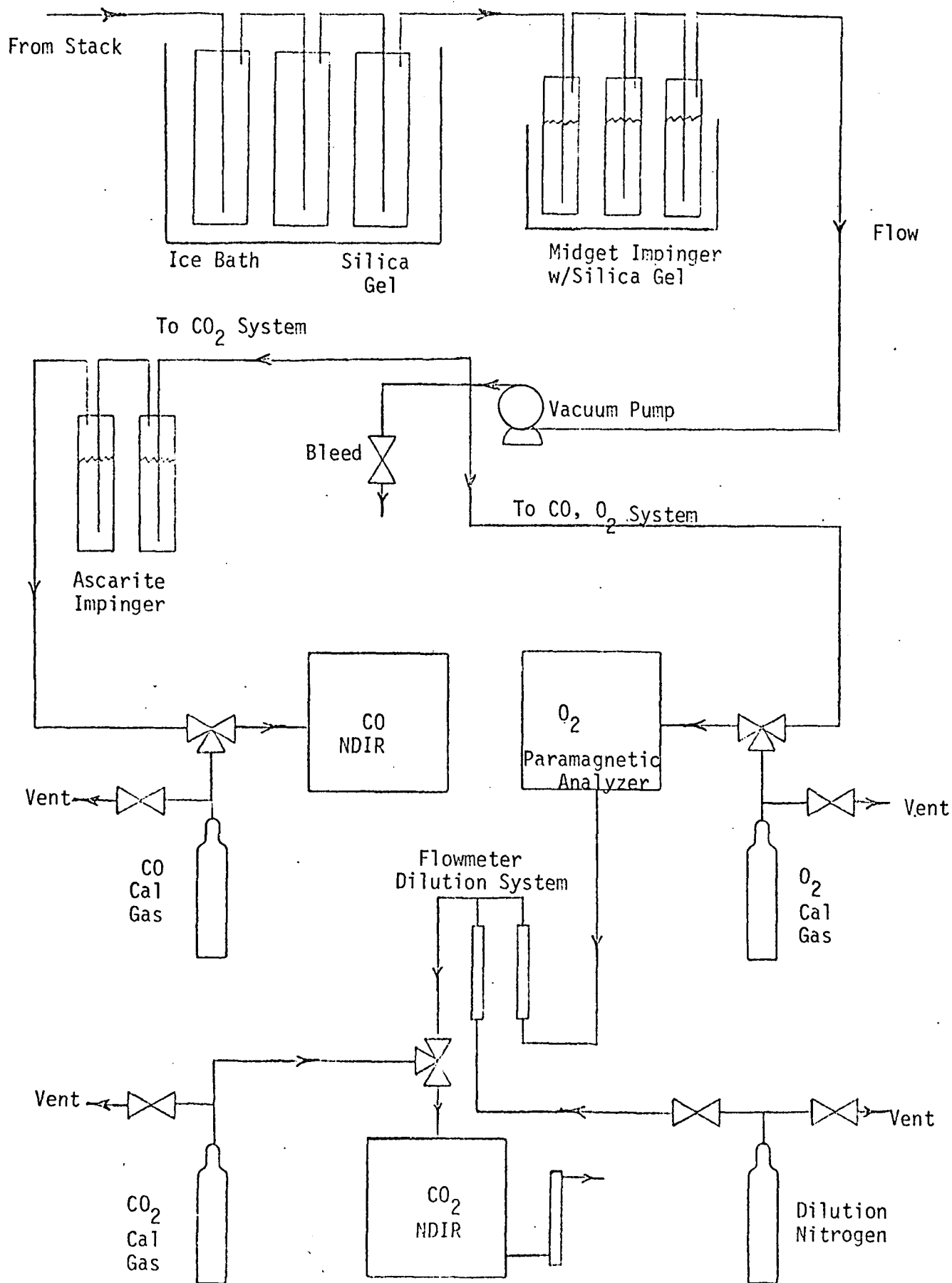
Container No. 5 - The spent silica gel was weighed at the site and recorded.

The filter from Container No. 1, and the beakers from Containers No. 2 and 3 for each run were sent to the EPA project officer after the initial analysis for additional analyses.

Sampling System for Oxygen, Carbon Dioxide, and Carbon Monoxide

Figure 7 is a schematic diagram of the sampling system.

Source gases were drawn continuously through a glass-lined probe and polyethylene tubing to a moisture trap consisting of silica gel impingers immersed in an ice bath. Valves on the pressure side of the vacuum pump controlled the flow of sample gas to the detectors. A bleed valve was provided to maintain adequate purging of the sample line. Gases to the oxygen and carbon monoxide detectors were passed through an ascarite bed to remove carbon dioxide which potentially interferes with the NDIR determination of carbon monoxide. Sample to the carbon dioxide detector was diluted with nitrogen to accommodate the range requirements of the detector.



CO₂, O₂, and CO SAMPLING SYSTEM

Figure 7

A Beckman model F-3 paramagnetic oxygen analyzer capable of measuring 0 - 25% oxygen was used for O_2 detection. Beckman NDIR models 315-B and 315-A, respectively, were used in determining carbon dioxide and carbon monoxide concentrations. The instrument configurations were 0 - 5% CO_2 and 0 - 1000ppm CO. All instruments were supplied with a low, medium and high range which were calibrated separately. The detectors were switched on and allowed to run continuously 24 hours per day for the entire sampling interval.

Calibration

All calibration gases were supplied and analyzed by Matheson Gas Products, Inc., Morrow, Georgia, and La Porte, Texas. The calibration procedure was conducted prior to sampling each morning and was repeated at the end of each day. Nitrogen was introduced into each instrument and the zero control was adjusted to obtain a steady "zero trace" on the recorder. Appropriate standards were then passed into the instruments at less than 100 cc/minute. The gain controls for each range were adjusted to provide maximum deflection and accuracy.

Daily Operation

Each morning after calibrating the instruments, charging the traps, and checking the probe, the system was assembled as shown in Figure 7. The dilution to the carbon dioxide detector was regulated to provide an accurate deflection range at a total flow rate less than 100 cc/minute. Flows for sample gas and dilution nitrogen were measured with a bubble tube. The recorder traces were observed and the ranges

were adjusted throughout the sampling interval as required. Occasionally sampling was interrupted to obtain odor samples, charge traps, or to check the system.

Sampling Procedure for Nitrogen Oxides

Nitrogen oxide concentrations of the recovery furnace outlet gases were determined by using the EPA Method 7, which is described in the Federal Register (Volume 36, No. 247, December 23, 1971).

Essentially, the method consisted of collecting a grab sample of the gas in an evacuated 2-liter flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution. The sample remained in the flask at least 16 hours, and was then placed in a glass storage bottle. Sodium hydroxide (1N) was then added to the sample until alkaline. The samples were taken back to the laboratory in Gainesville, Florida, and measured colorimetrically using the phenoldisulfonic acid procedure.