United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EMB Report 79-OCM-16
February 1981

Air

EPA

Synthetic Organic Chemical Manufacturing Industry
Dimethyl Terephthalate

Emission Test Report
Hercofina
Wilmington, North Carolina

SOURCE TEST AT HERCOFINA

DIMETHYL TEREPHTHALATE PLANT

WILMINGTON, NORTH CAROLINA

Contract No. 68-02-2812

Work Assignment 54

Technical Manager: Winton Kelly

Prepared for:

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

Prepared by:

TRW
ENVIRONMENTAL ENGINEERING DIVISION
P. O. Box 13000
RESEARCH TRIANGLE PARK, N. C. 27709

TABLE OF CONTENTS

GLOSSARY OF TERMS

TGNMO - Total Gaseous Non Methane Organics
THC - Total Hydrocarbon
FID - Flame Ionization Detector
TCD - Thermal Conductivity Detector
GC - Gas Chromatograph
ppm - parts per million
RT - Retention Time
VOC - Volatile Organic Compound
CM - Continuous Monitor

SAMPLE IDENTIFICATION GLOSSARY

H - Hercofina Plant
T - TGNMO Sample
B - Integrated Bag Sample
O - Outlet Location
I - Inlet Location

ex. HTO - 2 is Hercofina TGNMO sample taken at the outlet 2nd Run.

1.0 INTRODUCTION

During the period of November 26 through November 30, 1979, personnel from TRW Environmental Engineering Division conducted tests of a Dimethyl Terephthalate plant at Hercofina Inc., Wilmington, North Carolina. Personnel from the Environmental Protection Agency's Emission Measurement Branch (EPA/EMB) were present to monitor and observe the testing. The collection and review of process information during testing was carried out by personnel from Energy and Environmental Analysis, Inc. (EEA), Durham, North Carolina under contract to EPA.

The purpose of the testing was to obtain and analyze samples to provide data in support of possible New Source Performance Standards (NSPS) for synthetic organic chemical manufacturing and to develop background information regarding carbon adsorption techniques used for VOC emission control. Sampling was performed at the inlet and outlet of the carbon adsorber for the determination of the adsorber efficiencies. The carbon adsorber serves the "C" line, Dimethyl Terephthalate (DMT) oxidation vessel. Levels of Volatile Organic Compounds (VOC) were monitored utilizing three differing techniques (TGNMO, Method 25; FID continuous monitor, and GC/FID total hydrocarbon) to develop information for selecting an appropriate testing procedure for this type source.

The emissions were analyzed for total hydrocarbons, methyl acetate, methyl alcohol, benzene, toluene, xylenes, formic acid and acetic acid. In addition, the gaseous samples were analyzed for CO_2, O_2, N_2, and CO.

All of the testing took place at the Hercofina plant in Wilmington, North Carolina by TRW personnel. The analysis was also conducted at this site with the exception of the TGNMO cylinders which were sent to Pollution Control Science, Inc., Miamisburg, Ohio for analysis.

The initial test request included obtaining samples of the liquid from the stripping steam condensate. This sampling location was inaccessible at the time of the test and therefore no samples were collected.

2.0 SUMMARY AND DISCUSSION OF RESULTS

Sampling at the Hercofina plant took place at the inlet and outlet of the carbon absorber. Samples were collected by placing a steam heated manifold at the two locations and extracting three gas streams. The first stream was pumped through a long length of polypropylene tubing to the continuous monitoring shed where it was monitored by a continuous Flame Ionization Detector (FID) for total hydrocarbons. The second stream was metered into a tedlar bag (EPA Method 110) and provided a one-hour integrated sample for GC/FID analysis. The manual procedure for EPA Method 25 (TGNMO) was utilized on the third stream. These samples were taken at the inlet (Figure 2.1, point A) and at the outlet (Figure 2.1, point B) simultaneously.

Three sets of samples were taken and are represented graphically in Figure 2.2. Both the inlet and outlet of the absorber are listed. Carbon absorber bed A and bed B alternated to provide better absorption efficiencies. Each bed built up with hydrocarbons and at a certain level the bed was reactivated with steam purging. This relationship is evident graphically in the total hydrocarbon analysis plotted versus time. Figure 2.3 represents the integrated bag sample analysis and the TGNMO analysis. The relative times these samples were obtained are shown on the top of Figure 2.2. The individual component analyses of the integrated bag samples are presented in Table 2.1. The TGNMO analysis is presented in Table 2.2.

The apparent efficiencies of the carbon absorber are listed in Table 2.3. As can be seen from this table, there is a great variation in results. The percent moistures are listed below the table which would account for most of this deviation in the TGNMO analysis. The moisture problem is detailed in the sample line problems in Section 5.

The continuous monitor data has not taken into account the varying response factors of differing compounds. The response factors are calculated in the bag analysis and are presented in Appendix A.

The data gained from this test shows inconsistency of results between test runs and test methods. No attempt was made to determine the specific reasons for these variations by additional testing and/or experiments as to the validity of the individual methods used. The results as achieved by this one test cannot be used to select and support an appropriate test procedure for this type source.

TABLE 2.1 GAS ANALYSIS

	COMPONENT RUN	HBI - 1	HBO - 1	HBI - 2[d]	HBO - 2
a	METHYL ALCOHOL	4.90	190		0
a	METHYL FORMATE	917	921		752
a	METHYL ACETATE	632	127		85
a	OTHER	20	128		15
b	BENZENE	119	6.4		6
b	TOLUENE	982	36		34
b	XYLENE	6736	385		455
	TOTAL HC PPM	9411	1793		1347
	%M	5.66%	3.76%		3.76%
	FIXED GASES[c]	97.10	99.73		100.78
	TOTAL %	103.70	103.67		104.67

[a]PPM AS METHANE; SHIMADZU MINI - 2 DUAL FID (POROPAK - Q)
[b]PPM AS METHANE; SHIMADZU MINI - 1 DUAL FID (SP - 1000)
[c]%v/v; SHIMADZU 3BT (MOLECULAR SEIVE, CHROMOSORB 102)
[d]SAMPLE BAG EXPLODED

TABLE 2.1 GAS ANALYSIS (CONTINUED)

	COMPONENT RUN	HBI - 3	HBO - 3A	HBO - 3B	
a	METHYL ALCOHOL	3.8	206	4.2	
a	METHYL FORMATE	1921	848	396	
a	METHYL ACETATE	83.5	66	42	
a	OTHER	1286	181	174	
b	BENZENE	63	1.6	31	
b	TOLUENE	540	0	20	
b	XYLENE	8695	57	73	
	TOTAL HC PPM	12592	1359.6	740	
	%M	5.0	2.21	2.21	
	FIXED GASES[c]	91.76	93.11	99.85	
	TOTAL %	98.02	95.45	102.13	

[a]PPM AS METHANE; SHIMADZU MINI - 2 DUAL FID (POROPAK - Q)
[b]PPM AS METHANE; SHIMADZU MINI - 1 DUAL FID (SP - 1000)
[c]%v/v; SHIMADZU 3BT (MOLECULAR SEIVE, CHROMOSORB 102)

TABLE 2.1 GAS ANALYSIS (CONTINUED)

	COMPONENT RUN	HBI - 4	HBO - 4		
a	METHYL ALCOHOL	13.4	94		
a	METHYL FORMATE	324	425		
a	METHYL ACETATE	276	87		
a	OTHER	14	12		
b	BENZENE	58.8	5.2		
b	TOLUENE	0	10.8		
b	XYLENE	304	143		
	TOTAL HC PPM	990	777		
	%M	3.7	4.9		
	FIXED GASES[c]	94.4	92.75		
	TOTAL %	98.2	97.73		

[a]PPM AS METHANE; SHIMADZU MINI - 2 DUAL FID (POROPAK - Q)
[b]PPM AS METHANE; SHIMADZU MINI - 1 DUAL FID (SP - 1000)
[c]%v/v; SHIMADZU 3BT (MOLECULAR SEIVE, CHROMOSORB 102)

TABLE 2.2: TGNMO ANALYSIS

PCS SAMPLE #	SAMPLE I.D.	SAMPLE VOLUME (L)	PPM C_1 TRAP	WEIGHTED TANK AVG. PPM C_1	PPM C_1 TANK	TOTAL PPM C_1	TOTAL MG/L C_1	TANK #	TRAP #
93816	HTI-1	3.549	76720	5102	4198	81838	40.862	86	7
93816	HTI-1	3.990			5906			71	
93817	HTO-1	3.800	1658	2638	3165	4307	2.150	96	10
93817	HTO-1	3.758			2106			76	
93818	HTI-2	4.092	32757	2074	806	37288	18.618	95	11
93818	HTI-2	3.773			3450			77	
93819	HTO-2	3.885	11027	1568	1950	12595	6.289	F306	12
93919	HTO-2	3.671			1163			F162	
93820	HTI-3	5.471	38945	660	402	39605	19.775	F312	9
93820	HTI-3	5.449			920			F117	
93821	HTO-3	4.684	1123	762	408	1885	0.941	F320	4
93821	HTO-3	4.830			1106			F314	

Table 2.3. CARBON ABSORBER EFFICIENCIES

	TGNMO*	Bag*	CONT*
		Run #1	
Inlet	81838	9631	N/D
Outlet	4307	1737	1037
Efficiency (%)	94.7	82.0	--
Moisture (%)	3.76	3.76	3.76
		RUN #2	
Inlet	37288	N/D	8036
Outlet	12595	1370	1019
Efficiency (%)	66.2	--	87.3
Moisture (%)	4.35	4.35	4.35
		RUN #3	
Inlet	39605	12634	6462
Outlet	1885	1145	1369
Efficiency (%)	95.2	91.0	78.8
Moisture (%)	5.0	5.0	5.0
		RUN #4	
Inlet	N/S	3576	7918
Outlet	N/S	790	1641
Efficiency (%)	N/S	77.9	79.3
Moisture (%)	4.3	4.3	4.3

N/D - Not detected.

*All units in ppm as methane.

N/S - Not sampled.

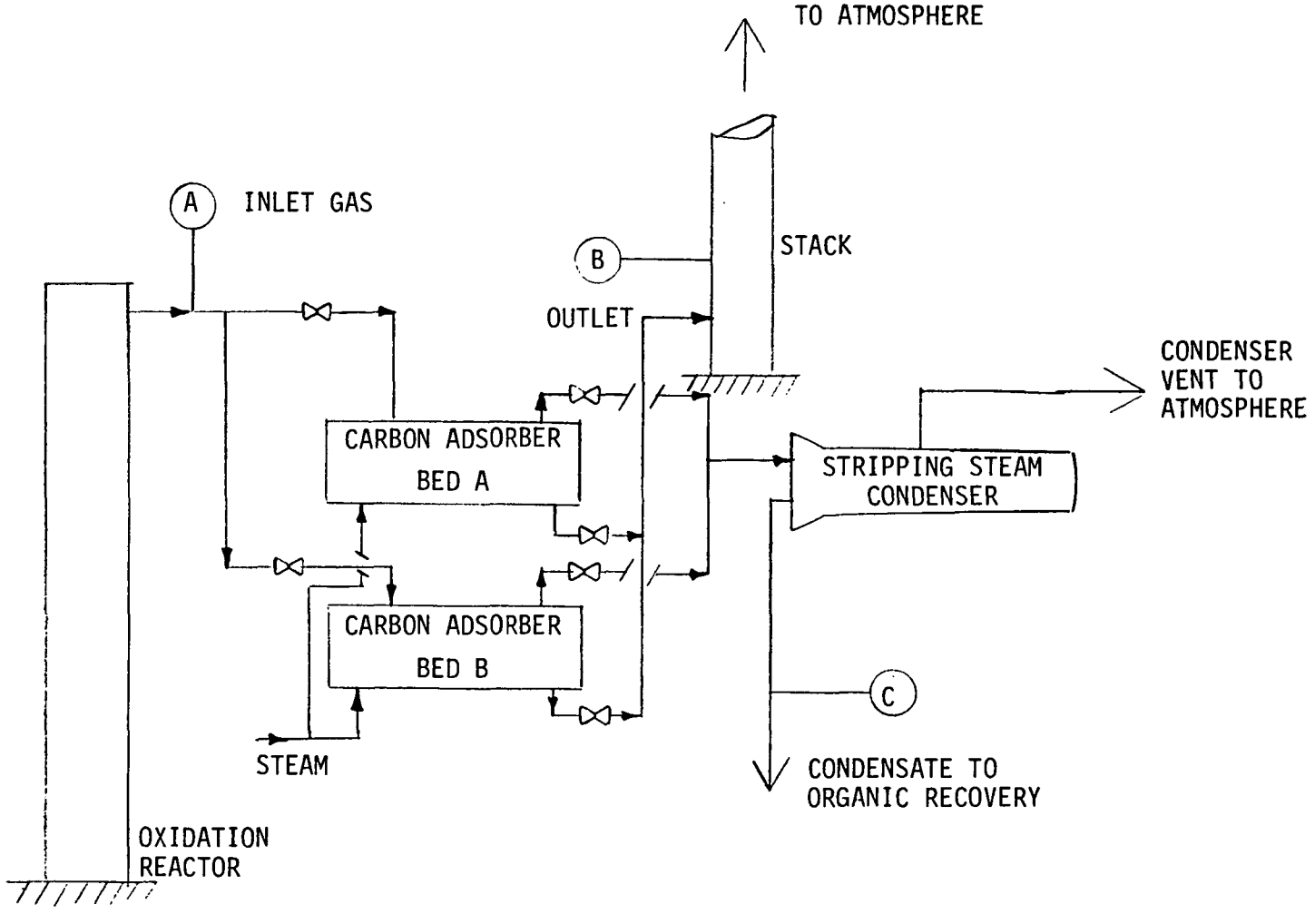

FIGURE 2.1: Sample Locations, Hercofina Plant

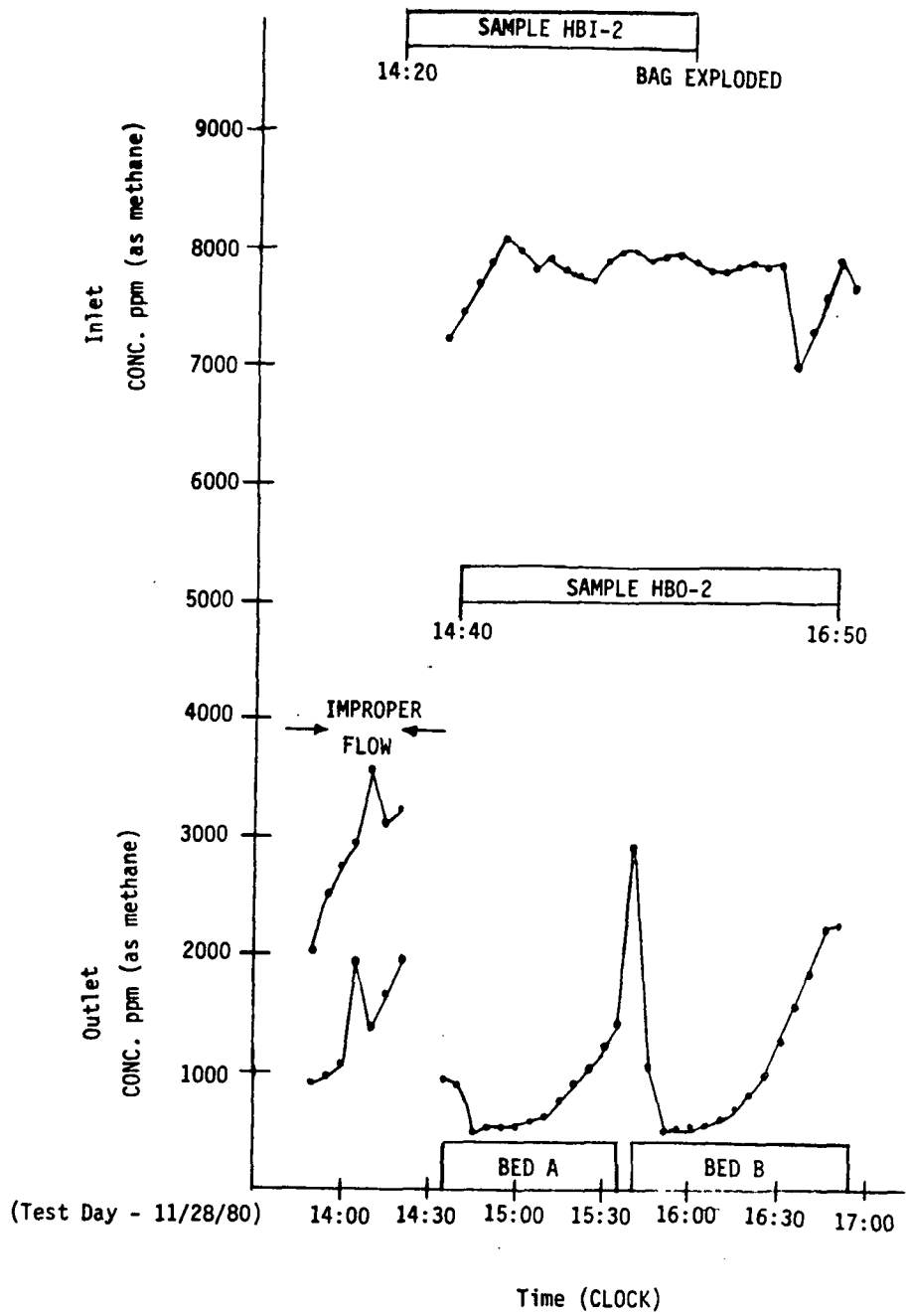

FIGURE 2.2: Inlet vs Outlet CM/FID Data (Run 2)

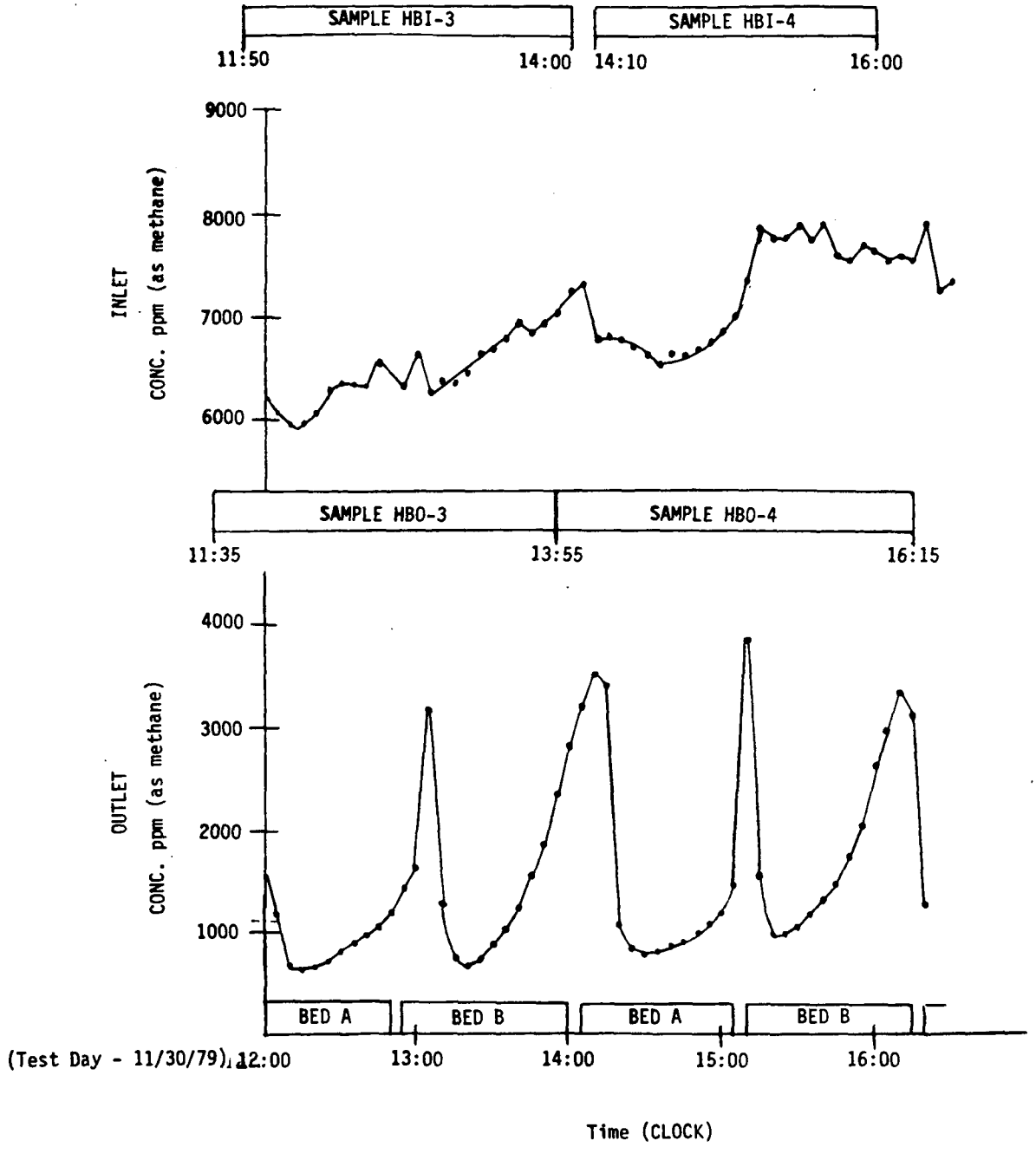

FIGURE 2.2: Inlet vs Outlet CM/FID Data (Run 3 and 4) (Continued)

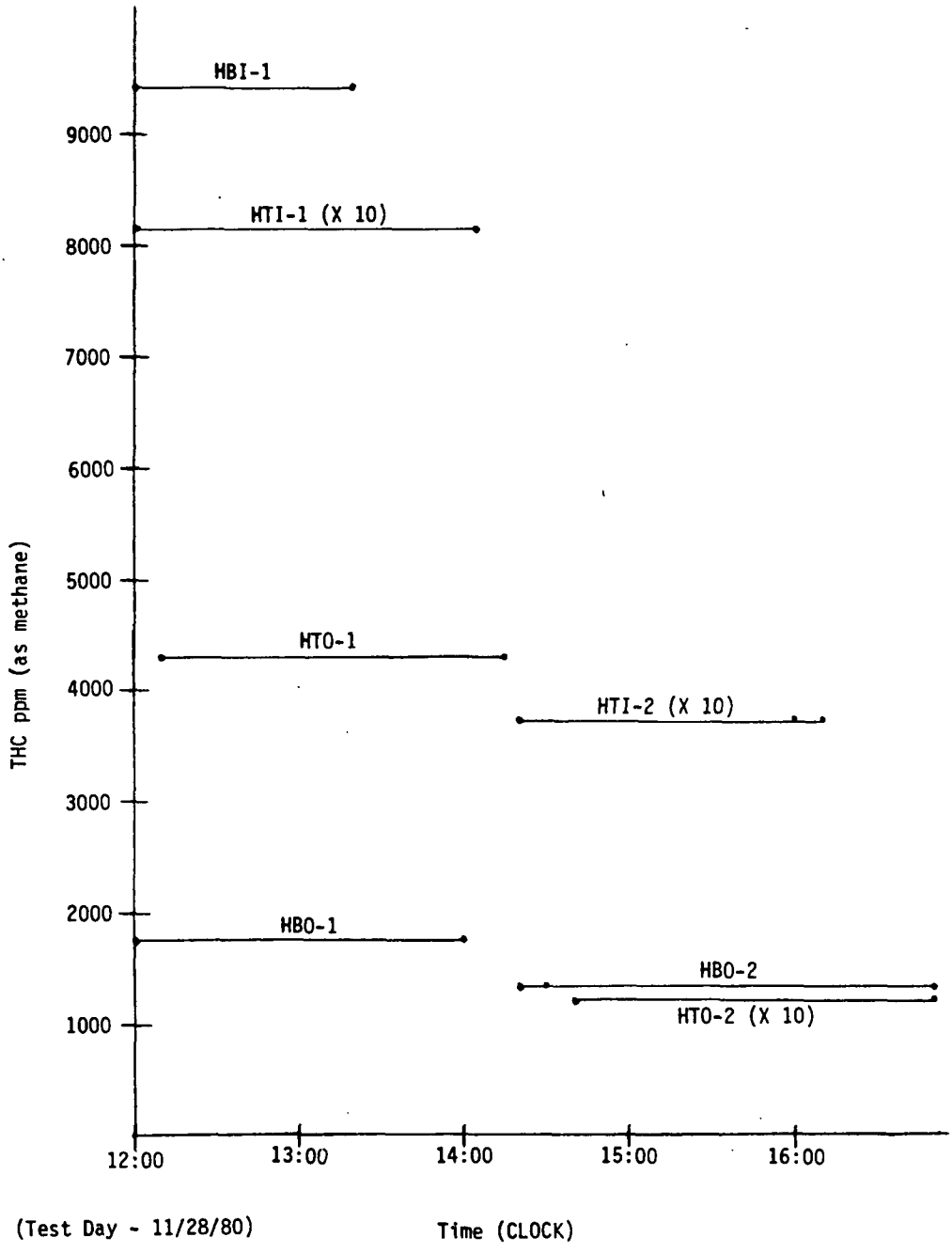

FIGURE 2.3: TGNMO vs Integrated Bag Analysis

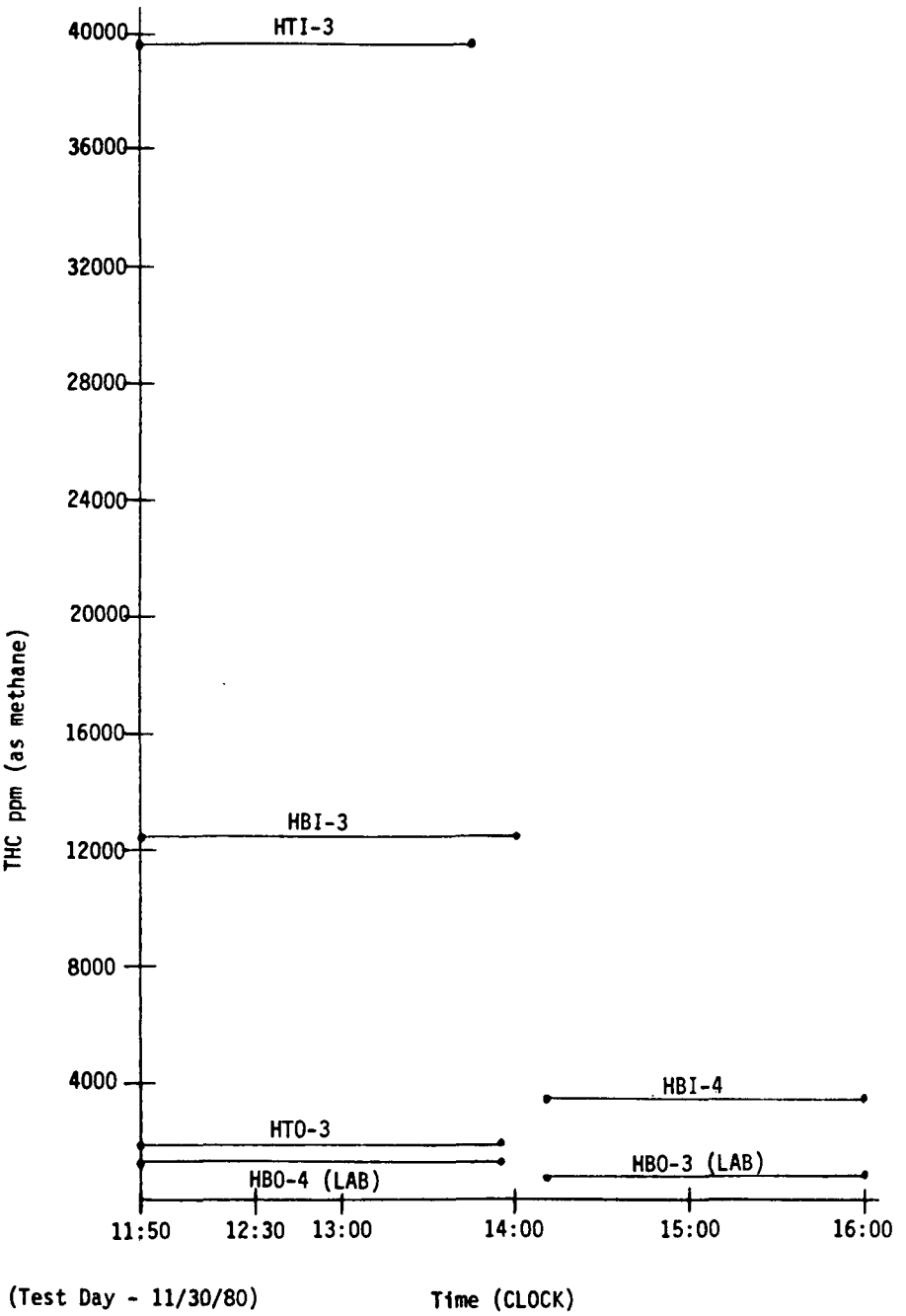

FIGURE 2.3: TGNMO vs Integrated Bag Analysis (Continued)

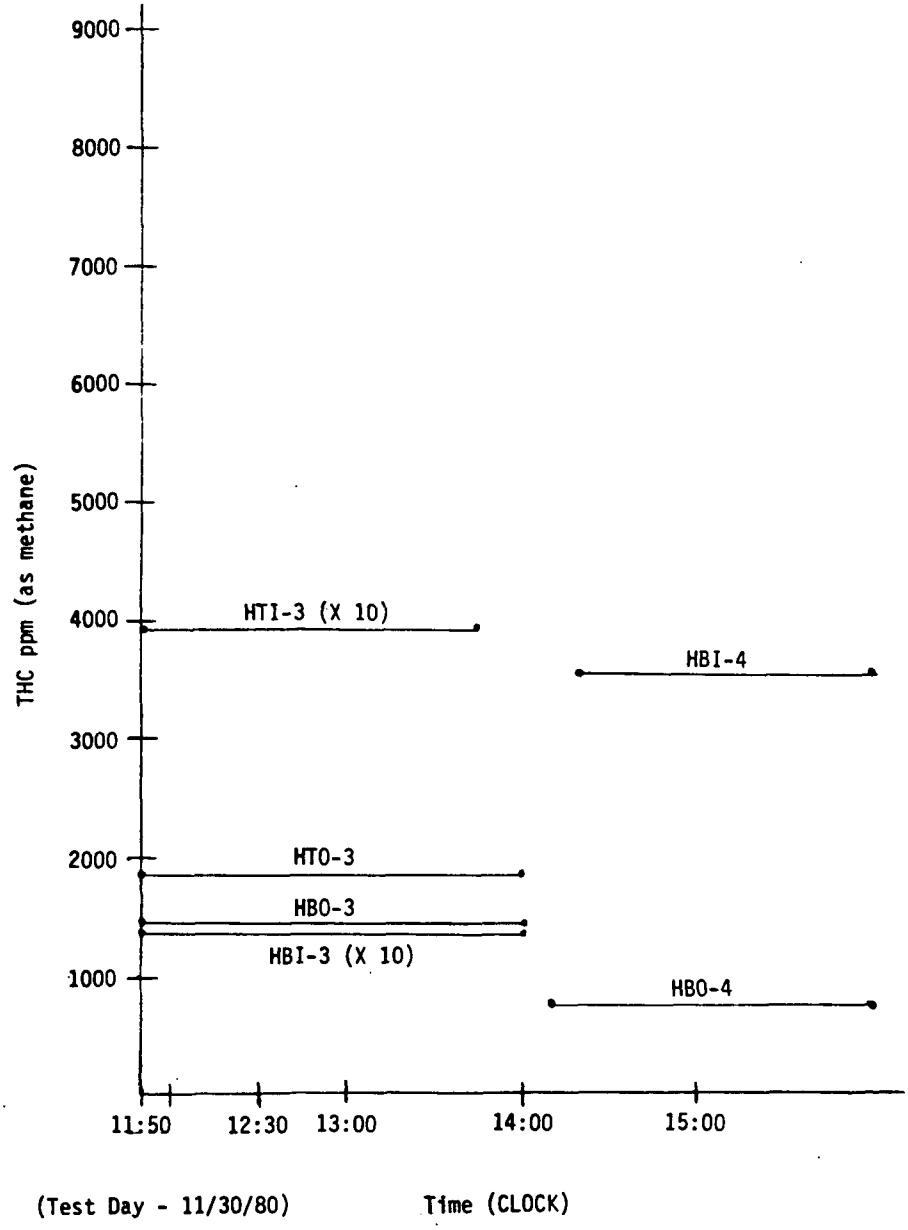

FIGURE 2.3: TGNMO vs Integrated Bag Analysis (Continued)

3.0 PROCESS DESCRIPTION

(to be supplied by EPA)

4.0 LOCATION OF SAMPLING POINTS

Sampling locations are presented schematically in the flow diagram (Figure 2.1). The locations are described in the following sections:

- 4.1 Carbon Adsorber Inlet
- 4.2 Carbon Adsorber Outlet

The sample points are shown specifically in Figure 4.1.

4.1 CARBON ADSORBER INLET

The carbon adsorber inlet position in the Hercofina process was located after the oxidation reactor and before the carbon bed systems. The sample pollutants of interest were defined as those emissions from the p-xylene and p-methyl toluate oxidation. The carbon adsorber sample inlet position (Figure 4.1) diagrams the sample point above the carbon beds. This position was on the second level of the process superstructure beside the top of the carbon beds. The sample port consisted of a ball valve port which had to be adapted with teflon tubing to the sample chamber. A steam line from the plant process was used to heat the sampling apparatus initially. However, sufficient control of heating could not be achieved, and tests two, three and four were run with no sample line heating.

4.2 CARBON ADSORBER OUTLET

The carbon adsorber outlet in the Hercofina process was located after the carbon bed system and before the stack. The sample stream was defined as the effluent of the carbon adsorption bed of unreacted p-xylene and low molecular weight hydrocarbons. This position is diagrammed in Figure 4.1 to be located below the carbon absorbers. The sample point was a ball valve port from the carbon bed exit pipe which was approximately five (5) feet from the ground level. The sample port

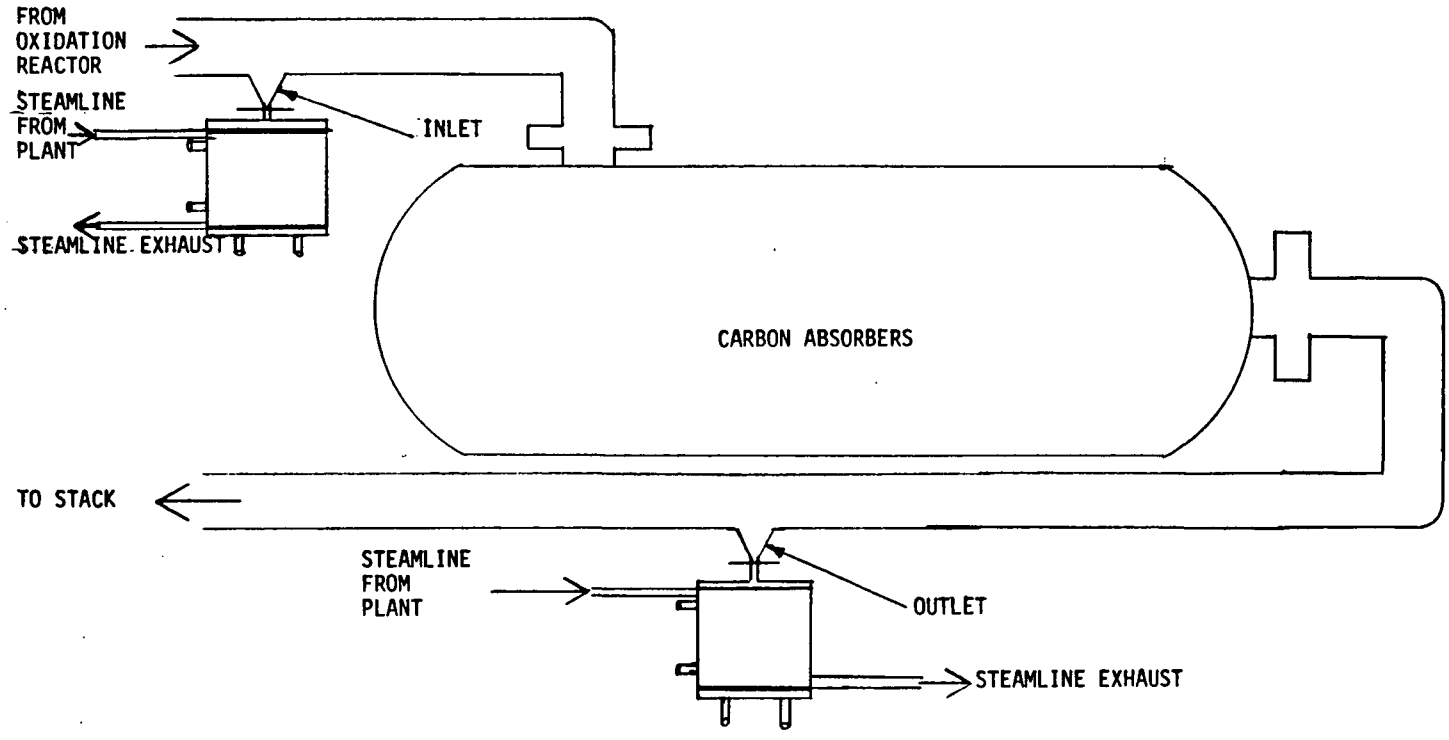

FIGURE 4.1: Carbon Absorber Sample Positions, Hercofina Plant

had to be adapted with teflon tubing to the sample chamber. A steam line from the plant process was used for the jacket of coils on the sample chamber. However, sufficient control of heating could not be achieved, and tests two, three and four were run with no sample line heating.

5.0 SAMPLING AND ANALYSIS PROCEDURES

5.1 SAMPLING AND ANALYSIS PROCEDURES

Three sampling systems were utilized for the detection of VOC's at the Hercofina plant and are represented schematically in Figure 5.1. Each system consisted of different modes for the collection of gaseous sample. The collection systems were (1) the Integrated Bag Method, (2) the Manual Sampling Method for EPA Method 25, and (3) the Continuous Monitor System. Each of the three systems were installed at the inlet and outlet of the carbon adsorber. The sample lines from each system were connected into a sample chamber (see Figure 5.2) from the sample location of the inlet and outlet; therefore, permitting the three systems to sample simultaneously. A fourth outlet of the sample chamber was used for the extraction of an EPA Method 4 sample for moisture determination taken during each run.

5.1.1 Integrated Bag Method (EPA Method 110)

Figure 5.3 illustrates the sampling apparatus used during testing. This system was chosen due to the explosion risk and safety requirements of the plant. The collection system consisted of a can which seals at a vacuum of 15" of mercury (Hg), a bag evacuated to 29" Hg, a flowmeter for metering gas, and teflon tubing to serve as a sample line.

The procedure was to evacuate the can with the outside self-sealing valve. After a vacuum was achieved, the can vacuum would be checked by placing a vacuum guage on the outside valve and monitoring the pressure. The can would be considered leak free if less than a 1" Hg pressure change was observed. The second step was to evacuate the bag to 29" Hg. The same leak check was made on the bag as the can. The flowmeter and can were then transported to the sample site and connected to the sample chamber and the sample system fabricated. The sample valve was opened

at the appropriate time and the sample extracted from the sample point. Proper flow was maintained with adjustment of the flowmeter.

5.1.2 Manual Sampling for EPA Method 25

The manual method for EPA 25 was used in the detection of Total Gaseous Non-Methane Organics (TGNMO). This method utilized at Hercofina is discussed in Attachment 2 of the Guideline Series: Measurement of Volatile Organic Compounds (EPA - 450/2-78-041). The equipment was prepared and provided by EPA personnel to the TRW field crew before the test. The sample system was fabricated in the TRW van and transported to the two sample locations. The system was connected into the sample chamber and the valve opened at the appropriate time. If the pressure of a sampling tank fell to zero, the tank would be changed immediately.

5.1.3 Continuous Monitor Flame Ionization Detector

The continuous monitor system was located in a room provided by the plant which was located approximately 100 feet from the carbon absorber inlet and outlet sample locations. A steam heated sample line from each sample point was set-up but could not be maintained throughout the test, due to the high steam temperature. Therefore, the sample lines were reconstructed without the steam heated hose for the remaining portion of the test. The continuous monitor set-up was according to EPA standards outline in the EPA document 450/2-78-041. This system (see Figure 5.1) utilized two separate FID's for the two sample locations. A Beckman 402 FID was positioned for analysis of the Carbon Absorber Inlet and a Horiba FID for the analysis of the Carbon Absorber Outlet.

5.1.4 The Sample Chamber

The sample chamber was constructed by TRW personnel before the test trip. This chamber was designed (see Figure 5.2) to permit four sampling systems to operate simultaneously at a single point. This was accomplished by connecting a line from the sample point into the chamber; therefore, the sampling systems could be connected into the chamber at the four outlets and operated simultaneously. The outlet allowed for the EPA Method 4 moisture determination train to be capped

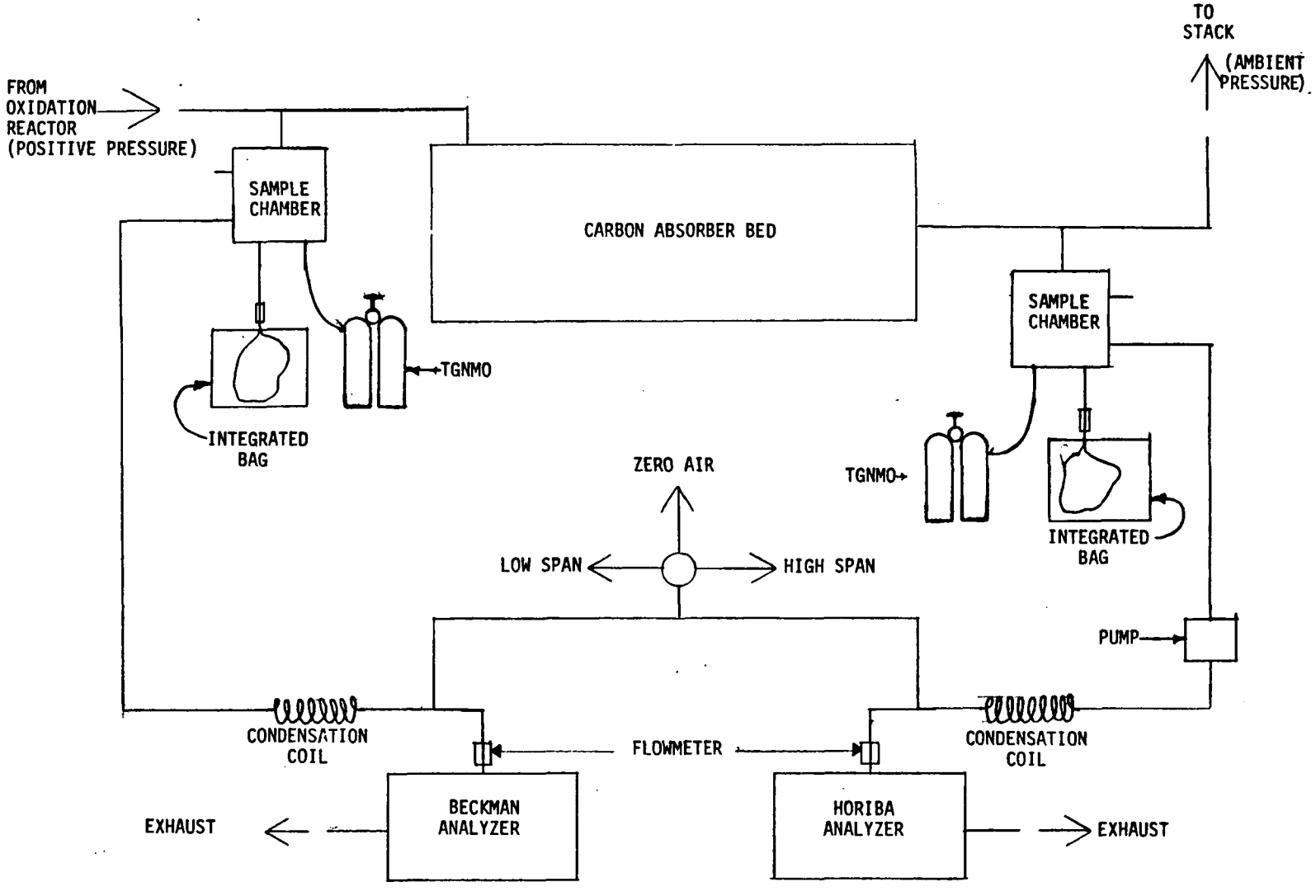

FIGURE 5.1: Sampling Systems Schematic, Hercofina Plant

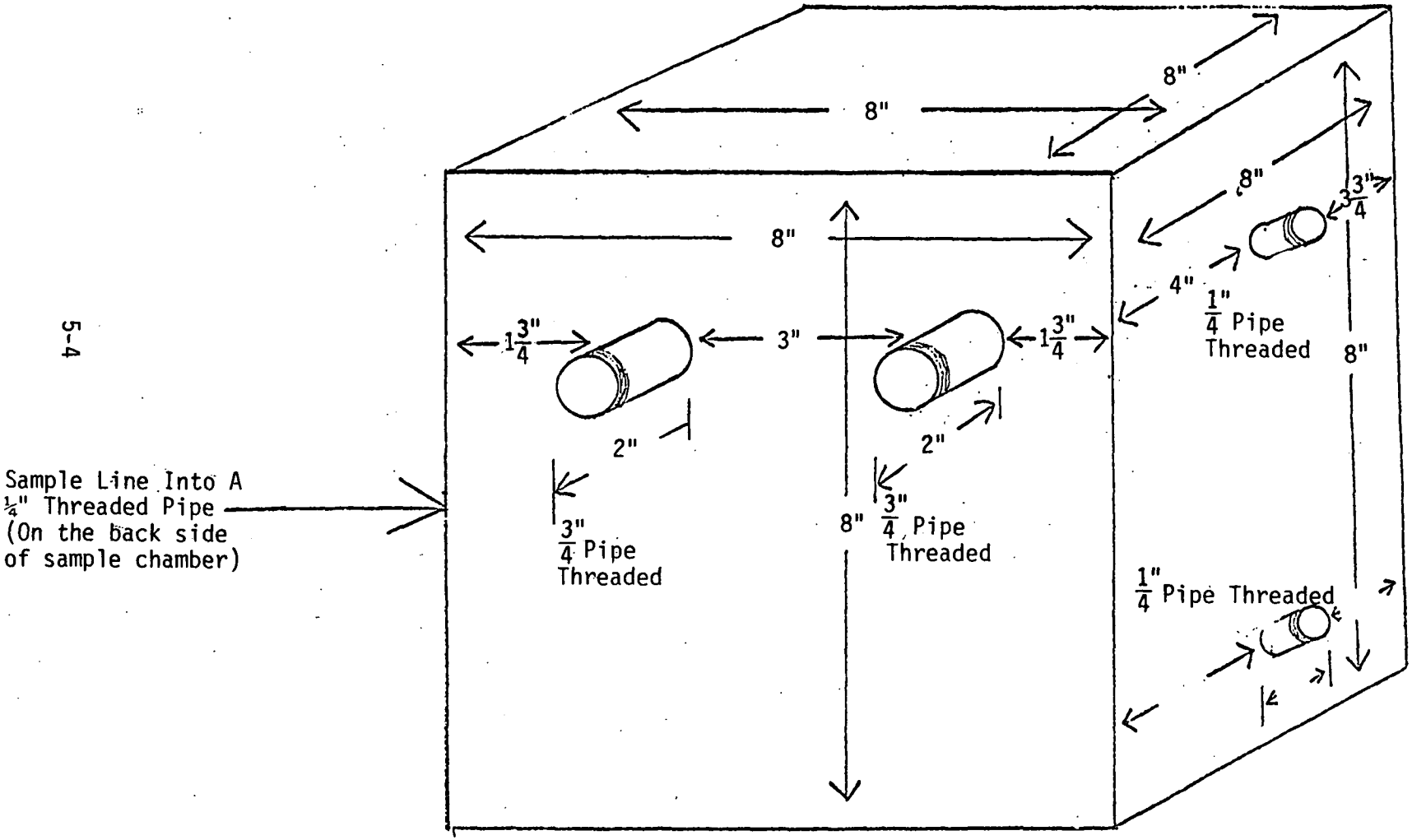

FIGURE 5.2 : Sample Chamber

off whenever this method was not being sampled. The temperature of the sample chamber was controlled with a steam line of copper tubing coiled around the chamber. The coils were insulated with abestos and sealed with tape.

5.1.5 Moisture Determination By EPA Method 4

The Method 4 train was assembled in the sampling van according to EPA Method 4. The system was then transported to the sample location and connected to the sample chamber. The sample was withdrawn from the sample chamber for 30 minutes and the data recorded. The sample was returned to the van and immediately processed.

5.2 ANALYTICAL PROCEDURES

The gas emissions from the carbon absorption unit were analyzed for seven (7) components. Methyl alcohol, methyl formate, methyl acetate, Benzene, toluene, ethyl benzene and xylenes.

5.2.1 Integrated Bag Analysis

A portable gas chromatograph (Shimadzu, Mini 2 Series) was used for the analysis of low molecular weight (C_1-C_6) compounds. The gas chromatograph was equipped with dual column-FID's for background correction and a two position gas injection valve. Separations were accomplished on a 6' X 1/8" stainless steel analytical column packed with Poropak Q. Column conditions are listed below:

Carrier:	Helium, 20 ml/min.
Oven Temp:	Isothermal at 75°C
Detector Temp:	175°C
Injector Temp:	25° 1 ml sample loop

An analyzed gas mixture in nitrogen (Scott Environmental) was used to establish the retention times of C_1-C_6 alkanes. The retention times as well as responses of methyl alcohol, methyl formate and methyl acetate were established by preparing standards of each individual compound at known concentrations. Response factors were determined for each compound relative to methane (Appendix B).

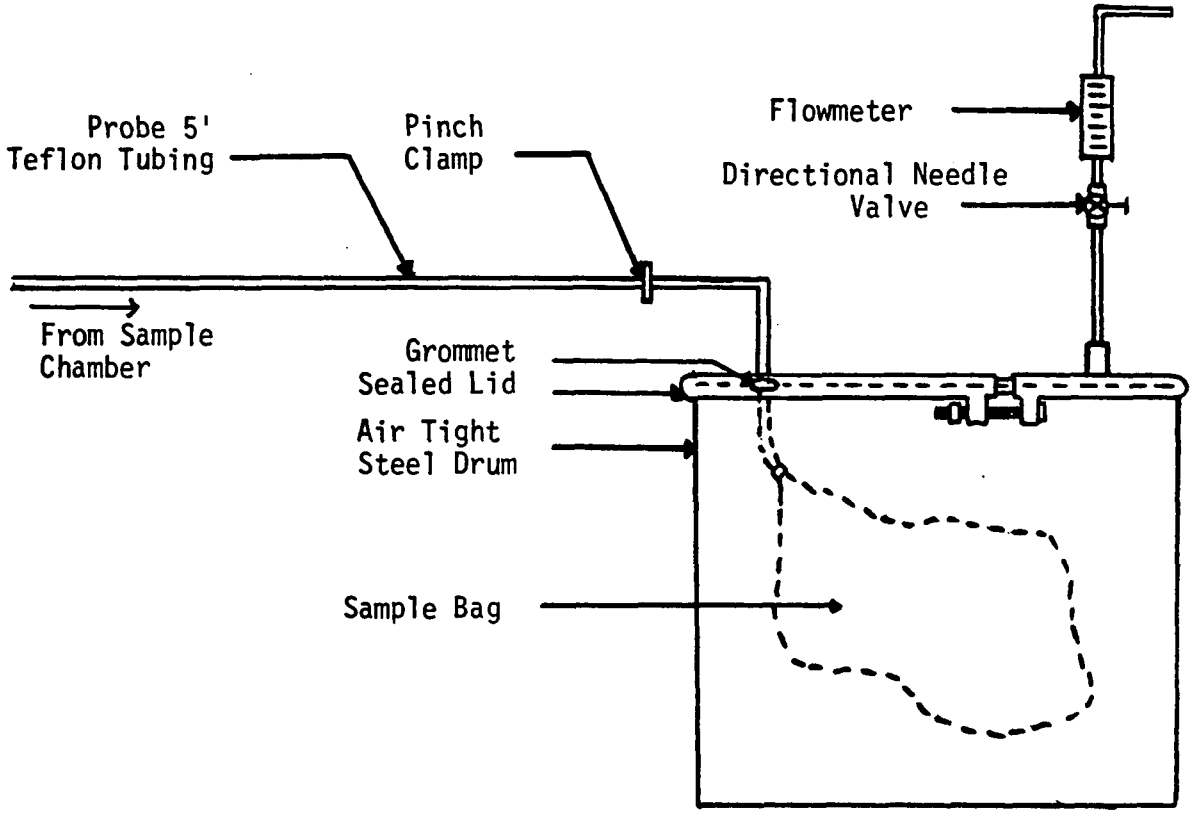

FIGURE 5.3: Integrated Bag Sampling System

A second GC (Shimadzu, Mini 1 Series) equipped with an FID detector was used for the analyses of the aromatic compounds, benzene, toluene, ethyl benzene and xylene. The column was a 6' X 1/8" stainless steel packed with SP-1000 on Supelcoport. Sample injection was accomplished with a sample injection valve with a 2 ml sample loop. Benzene standards covering the range of 10 to 500 ppm were prepared to check the detector linearity. Retention times and response of the substituted benzenes were established by preparing individual standards. Concentrations were determined by responsive factors related to benzene. Column conditions are given below:

Carrier:	Helium, 20 ml/min.
Oven Temp:	Programmed from 100 to 225°C @ 15°/min.
Detector Temp:	175°C
Injector Temp:	25°C

A third GC (Shimadzu 3BT) equipped with a portable thermal conductivity detector was used for the analyses of formic and acetic acids and N_2, O_2, CO, and CO_2. Sample injection was accomplished with a gas injection valve with a 1 ml sample loop. The column used was a 6' X 1/8" stainless steel packed with 15% SP 1220, 1% H_3PO_4 on Chromosorb WAW, 100/120 mesh and operated at 30°C isothermally. Standards for the organic acids were prepared in-house while the fixed gas standards were commercially prepared (Scott Environmental).

5.2.2 Total Gaseous Non-Methane Organics Analysis (TGNMO)

The equipment for the TGNMO (Method 25) sampling was provided by EPA. The initial conditions of the tanks and regulators are provided in Appendix B. The tanks and traps were stored after sampling by TRW. The traps were transported in dry ice to maintain the low temperature. The traps were transported in dry ice to maintain the low temperature. The traps and tanks were shipped by TRW to Pollution Control Science, Inc. (PCS) in Miamisburg, Ohio. David Robinson of PCS analyzed the samples according to EPA Method 25 presented in the Guideline Series: Measurement of Volatile Organic Compounds (EPA-450/2-78-041). This method is presented in Appendix D and the results from PCS presented in Section 2.

5.2.3 Continuous Monitor/Flame Ionization Detector Analysis (CM/FID)

The CM/FID system was set-up based on Attachment 3. Alternate Test Method for Direct Measurement of Total Gaseous Organic Compounds using a Flame Ionization Analyzer from EPA-450 2-78-041. This procedure is presented in Appendix D and was operated accordingly except for certain modifications. These modifications and an overall schematic of the CM/FID sample system is presented in Figure 5.1.

5.2.4 Moisture Determination

The moisture determination runs were conducted and analyzed according to EPA Method 4. The field sheets and calculations are presented in Appendix C.

5.2.5 Problems Encountered with Analyses

Two major problems were encountered in the analytical portion of this test. The first problem was the result of the analytical lab being set-up next to an electrical transformer room. This caused severe noise in one of the instruments (see Appendix B). This made analysis of samples very slow, hence, some of the samples were preserved and analyzed upon return to the lab in Raleigh. The major problem in this procedure results from the fact that the sample apparently degrades as a function of time.

The second problem was a result of cold ambient temperatures. Xylene constituents in a sample are affected by temperature, therefore, to minimize the effect, the samples were kept in a heated room until analysis, however, transfer from the sampling point to the analysis room could have resulted in a loss of xylene. The xylene standard was kept in a shed with the continuous FID and the temperature dropped below freezing during the night. This resulted in a 93% loss in the standard due to the cold temperature.