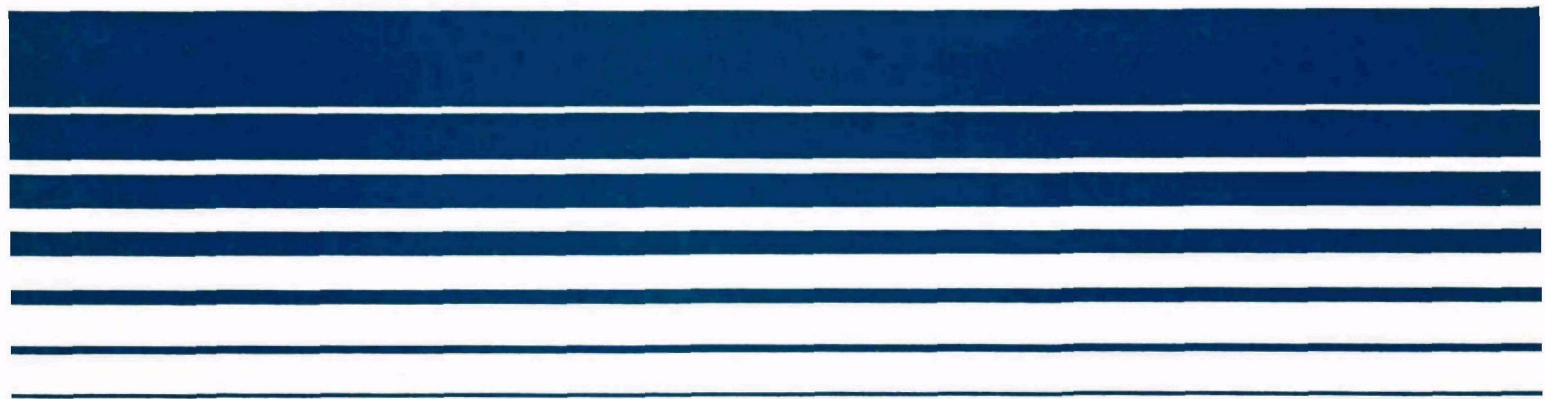


Air



# **Benzene Nitrobenzene Manufacture**

## **Emission Test Report E. I. Dupont De Nemours and Company Beaumont, Texas**



EMISSION TEST OF A NITROBENZENE PLANT AT E. I. du PONT de NEMOURS  
AND COMPANY, INC., BEAUMONT, TEXAS

by

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FINAL REPORT

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For

Emission Measurement Branch  
Field Testing Section  
Environmental Protection Agency  
Research Triangle Park, North Carolina 27711

Attn: Mr. J. E. McCarley, Jr.

## PREFACE

The work reported herein was conducted by Midwest Research Institute under Environmental Protection Agency (EPA) Contract No. 68-02-2814, Work Assignment No. 9.

The project was under the supervision of Mr. Doug Fiscus, Head, Field Programs Section, and Mr. William Maxwell, Program Manager. Mr. Maxwell served as field team leader and was assisted in the field by Messrs. George Scheil and Ron Jones, and Mr. Roy Neulicht of EPA, and in the lab by Messrs. George Scheil and Dennis Wallace and Ms. Alice Shan.

Approved for:

MIDWEST RESEARCH INSTITUTE



for L. J. Shannon, Executive Director  
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## SECTION 1

### INTRODUCTION

This report presents the results of source testing performed during the period September 25 to 29, 1978, by Midwest Research Institute (MRI) and the U.S. Environmental Protection Agency (EPA) on the nitrobenzene facility of E. I. du Pont de Nemours and Company, Inc., Beaumont, Texas. The portions of the process sampled were the waste acid and organic receivers coming from the process centrifuge. The waste acid receiver vapor stream was sampled before being vented to the aniline incinerator. The waste organic receiver vapor stream was sampled before and after the water scrubber. Samples were also obtained of the liquid effluent of the water scrubber.

The vapor streams were analyzed for benzene, nitrobenzene, total hydrocarbons (THC), and nitrogen oxides ( $\text{NO}_x$ ). Duct temperature, pressure, and flow rate measurements were also made on the two vapor streams prior to the control devices.

The results of these tests are to be evaluated by EPA as part of the development of emission standards for this industry.

## SECTION 2

### SUMMARY AND DISCUSSION OF RESULTS

The results of the analyses for benzene are given in Table 1. The benzene peak was found to contain an impurity during the field analyses (the peak was broader than normal). Further tests showed that benzene was present as a leading shoulder on a much larger peak. Later work showed that this larger peak is probably cyclohexane. It is assumed that this leading shoulder is benzene. It must be pointed out that later tests indicated that 1-methyl cyclopentene cannot be resolved from benzene on the column used. However, the presence of this compound is doubtful in this process. The location of the benzene peak was proved by running mixtures of the sample gases with the benzene standard gases. The benzene data presented in Table 1 are reliable within the limits of the standard deviations shown. See Section 5 for a detailed description of the analytical technique used. The mass emission rates for Tables 1 to 3 are of limited accuracy due to the inaccuracy of the measured flow rates.

The nitrobenzene peaks had a significant tailing on the column used. To obtain the most representative data, the areas were measured by cutting and weighing the peaks for nitrobenzene and the benzene standards. These results are given in Table 2. The relative constancy of the concentrations, except for No. 2 on the September 28 test, indicates that this component may be limited by vapor pressure in these samples. Extrapolation of data from Lange's Handbook of Chemistry indicates that at 20°C the expected vapor concentration of nitrobenzene is about 400 ppm. The results in Table 2 are reported as benzene. However, the response factor for nitrobenzene versus benzene was determined to be  $1.0 \pm 10\%$  by injection of known amounts of liquid into bags filled with measured volumes of nitrogen.

Table 3 shows the THC results for each sample obtained by a short empty column direct into the flame. Both benzene and propane standards were used. Measurements were by peak height.

Table 4 shows the concentrations of all the observed peaks in the chromatograms expressed as benzene. These measurements were by peak area, determined as peak height times width at one-half the height. Since some of the peaks were distorted, other measurement techniques such as planimetry or cutting and weighing of the chromatograms would be expected to yield more accurate results; however, these techniques are time consuming. An example is the differences in the results by the different methods for nitrobenzene (peak 20) as shown in the results of Tables 2 and 4.



TABLE 1. SUMMARY OF BENZENE RESULTS OF INTEGRATED BAG SAMPLES<sup>a/</sup>

Date	Site	Concentration <sup>b/</sup> ppm as benzene concentration, std. deviation	Average	Emission rate <sup>c/</sup> as benzene		gram Benzene emitted/megagram aniline produced
				lb/hr	kg/hr	
September 26	No. 1 - organic receiver scrubber inlet	490 ± 75 600 ± 135	545	0.0917	0.0416	2.65 <sup>d/</sup>
	No. 2 - organic receiver scrubber outlet	590 ± 90 500 ± 110	545	0.0917	0.0416	2.65 <sup>d/</sup>
	No. 3 - acid receiver vapor stream	230 ± 38 205 ± 41 200 ± 110	210	0.4625	0.2098	13.39 <sup>d/</sup>
September 27	No. 1	650 ± 69 680 ± 39 460 ± 86	595	0.1001	0.0454	2.90 <sup>d/</sup>
	No. 2	540 ± 47 590 ± 69	565	0.0950	0.0431	2.75 <sup>d/</sup>
	No. 3	175 ± 46 130 ± 46	150	0.3303	0.1498	9.56 <sup>d/</sup>
September 28	No. 1	130 ± 80 110 ± 33 160 ± 87	135	0.0227	0.0103	1.31 <sup>e/</sup>
	No. 2	190 ± 110 285 ± 56 140 ± 37	205	0.0345	0.0156	1.99 <sup>e/</sup>
	No. 3	95 ± 50 65 ± 45	80	0.1762	0.0799	10.20 <sup>e/</sup>

<sup>a/</sup> Condensate trap installed prior to integrated bag. See Table 7 and Section 5 for discussion.

<sup>b/</sup> Peak believed to be benzene but could also be 1-methyl cyclopentene. See Section 5 for description of measuring method.

<sup>c/</sup> All mass emission data calculated using the average flow rate (Table 9) for each test site.

<sup>d/</sup> Production rate is 107,100 Mg/yr aniline based on data supplied by the company. See Section 3 of this report.

<sup>e/</sup> Production rate is 53,550 Mg/yr aniline.

TABLE 2. SUMMARY OF NITROBENZENE RESULTS OF INTEGRATED BAG SAMPLE<sup>a, b/</sup>

Date	Site	Concentration <sup>c/</sup> ppm as benzene	Emission rate as benzene		gram Nitrobenzene emitted (as benzene)/Megagram aniline pro- duced
			lb/hr	kg/hr	
September 26	No. 1 - organic receiver scrubber inlet	260	0.0437	0.0198	1.26
	No. 2 - organic receiver scrubber outlet	289	0.0486	0.0220	1.40
	No. 3 - acid receiver vapor stream	210	0.4625	0.2092	13.39
September 27	No. 1	258	0.0434	0.0197	1.26
	No. 2	292	0.0491	0.0223	1.42
	No. 3	285	0.6276	0.2840	18.16
September 28	No. 1	246	0.0414	0.0188	2.40
	No. 2	82	0.0138	0.0063	0.80
	No. 3	340	0.7487	0.3387	43.33

<sup>a/</sup> Nitrobenzene results are reported as benzene. Instrument response factor for nitrobenzene was determined to be within 10% of the instrument response to benzene.

<sup>b/</sup> Condensate trap installed prior to integrated bag. See Table 7 and Section 5 for discussion.

<sup>c/</sup> Concentration determined by cutting and weighing the chromatograms for benzene standard and the nitrobenzene peak and comparing.

TABLE 3. SUMMARY OF TOTAL HYDROCARBON (THC) RESULTS OF INTEGRATED BAG SAMPLES<sup>a,b/</sup>

Date	Site	Concentration		Emission rate				gram Total Hydrocarbons emitted (as benzene)/megagram aniline produced
		As benzene (ppm)	As propane (ppm)	As benzene		As propane		
				lb/hr	kg/hr	lb/hr	kg/hr	
September 26	No. 1 - organic receiver scrubber inlet	7,520	9,320	1.26	0.57	0.88	0.40	36.37
	No. 2 - organic receiver scrubber outlet	7,970	9,870	1.34	0.61	0.94	0.43	38.92
	No. 3 - acid receiver vapor stream	3,140	3,890	6.92	3.14	4.84	2.20	200.34
September 27	No. 1	8,100	11,400	1.36	0.62	1.08	0.49	39.56
	No. 2	6,440	9,050	1.08	0.49	0.86	0.39	31.26
	No. 3	3,880	5,460	8.54	3.87	6.78	3.08	246.92
September 28	No. 1	6,210	8,580	1.05	0.48	0.81	0.37	61.25
	No. 2	6,210	8,580	1.04	0.47	0.81	0.37	59.97
	No. 3	3,360	4,640	7.40	3.36	5.77	2.62	428.74

<sup>a/</sup> Measured by peak height.

<sup>b/</sup> Condensate trap installed prior to integrated bag. See Table 7 and Section 5 for discussion.

TABLE 4. SUMMARY OF GENERAL RESULTS,<sup>a/</sup> PPM AS BENZENE

Peak No.	Site		
	No. 1 <sup>b/</sup>	No. 2 <sup>c/</sup>	No. 3 <sup>d/</sup>
September 26			
1	4.6	3.6	3.6
2		1.7	0.2
3	6.4	2.2	0.5
4	34.6	28.7	4.7
5	40.6	33.9	8.5
6	9.7	8.1	2.4
7	2,110	1,490	547
8	199	85.2	167
9	251	145	53.1
10	1,480	1,230	430
11, 11a <sup>e/</sup>	1,830	1,530	703
12	465	250	126
13	615	355	189
14	-	-	-
15	132	109	53.9
16	271	306	116
17	108	84.5	52.4
18	45.8	42.3	33.3
19	-	-	-
20 <sup>f/</sup>	232	200	141
Total	7,830 (104%)	5,910 (74%)	2,630 (93%)
THC result (from Table 3)	7,520	7,970	3,140

(continued)

TABLE 4. SUMMARY OF GENERAL RESULTS,<sup>a/</sup> PPM AS BENZENE (continued)

Peak No.	Site		
	No. 1 <sub>b</sub> /	No. 2 <sub>c</sub> /	No. 3 <sub>d</sub> /
September 27			
1	4.2	4.6	1.8
2	1.2	1.3	-
3	0.6	1.3	-
4	26.3	23.3	3.7
5	27.0	25.9	5.2
6	5.7	6.6	1.9
7	1,140	1,220	412
8	48.0	73.2	22.4
9	130	122	43.1
10	1,100	952	407
11, 11a <sup>e/</sup>	1,450	1,270	632
12	276	193	105
13	133	108	150
14	-	-	-
15	127	101	52.6
16	233	199	138
17	107	91.5	49.6
18	47.6	38.7	31.8
19	0.9	-	-
20 <sup>f/</sup>	<u>149</u>	<u>142</u>	<u>149</u>
Total	5,010 (62%)	4,570 (71%)	2,060 (53%)
THC result (from Table 3)	8,100	6,440	3,880

(continued)

TABLE 4. SUMMARY OF GENERAL RESULTS,<sup>a/</sup> PPM AS BENZENE (continued)

Peak No.	Site		
	No. 1 <sup>b/</sup>	No. 2 <sup>c/</sup>	No. 3 <sup>d/</sup>
September 28			
1	3.0	2.7	2.1
2	1.0	0.8	-
3	0.9	0.8	-
4	19.1	18.5	3.5
5	22.6	20.0	4.5
6	6.3	5.8	1.1
7	1,340	1,170	397
8	81.3	73.9	22.9
9	141	122	40.9
10	885	867	354
11, 11a <sup>e/</sup>	1,320	1,220	574
12	210	195	105
13	443	345	192
14	7.1	-	-
15	120	111	57.5
16	279	248	148
17	96.1	110	68.8
18	70.1	55.2	45.3
19	3.3	-	-
20 <sup>f/</sup>	315	70.2	178
Total	5,360 (86%)	4,640 (75%)	2,190 (65%)
THC result (from Table 3)	6,210	6,210	3,360

<sup>a/</sup> Integrated bag sample analysis with condensate trap installed prior to the bag.  
See Section 5 for discussion.

<sup>b/</sup> Organic receiver scrubber inlet.

<sup>c/</sup> Organic receiver scrubber outlet.

<sup>d/</sup> Acid receiver vapor stream.

<sup>e/</sup> Sum of benzene and superimposed peak.

<sup>f/</sup> Nitrobenzene.

The two compounds of greatest interest to EPA were benzene and nitrobenzene, and these results are shown in Tables 1 and 2, respectively, using the more appropriate measurement techniques. The other compounds listed in Table 4 are provided as secondary information to this test program. Because of this secondary interest only, these data were reported using the much quicker method of data reduction. For comparison purposes, the nitrobenzene (peak 20) results in Table 4 were calculated using the same data reduction technique as was employed for the other peaks shown in Table 4. It should also be understood that all concentrations are reported as if each of these compounds was benzene; the instrument response factor for each of these compounds was not determined. Some typical chromatograms are shown in Appendix A. Some of the 60 hydrocarbons searched for possible identification of the various peaks are listed in Table 5. The retention indices for all of the compounds measured in the search are given in Appendix B.

Table 6 shows the results of analyses of the three scrubber water samples obtained during the test after extraction into carbon disulfide. The scrubber water flow rate was 34 liters/min (9 gal/min).

Table 7 compares the benzene, nitrobenzene, and THC results obtained from the integrated gas samples with the results of analyses of the composite samples obtained from the condensate traps in each of the sampling lines. The equivalent vapor concentrations represent the concentrations resulting from vaporizing the material in a volume of gas equal to the estimated total integrated gas volumes. The main conclusion from this table is that the vapor stream concentrations are similar on the inlet and outlet of the scrubber but the entrained liquid is greatly reduced by the scrubber.

Table 8 presents the results of the  $\text{NO}_x$  analyses. The value of these results is questionable as all of the sample lines contained liquid, possibly nitric acid. Twenty- to 200-fold dilutions were required for the analyses.

Table 9 presents a summary of the stack gas data used in the emission calculations for the other tables. The flow rate measurements have limited accuracy due to the liquid entrainment and the low  $\Delta P$  pitot readings. Therefore only an average for all 3 days is presented.

All field data (excluding TGNMO) may be found in Appendix C. Sample calculations are given in Appendix G.

During this test program emission testing was conducted for Volatile Organic Carbon (VOC) using a test method under development by the EPA. The test work was conducted by EPA personnel. The purpose of the tests was two-fold. First, hands-on experience with the method during actual field use was desired so that problem areas could be identified. Secondly, comparative data obtained with the TGNMO and integrated bag/THC sampling methods were desired. Since results from the two sampling procedures would be compared, simultaneous samples were conducted from the same sampling location.

TABLE 5. POSSIBLE PEAK IDENTIFICATIONS

Peak No.	Retention index	Possible component
1	100-200	Air, methane, ethylene, acetylene, ethane
2	300	Propylene, propane
3	400	Isobutane, 1-butene, 2-methylpropene, n-butane
4	480	2-Methylbutane
5	500	n-Pentane, 1-pentene, 2-methyl-1-butene
6	525	2,2-Dimethylbutane
7	550	4-Methyl-1-pentene, cyclopentane, 2-methyl-pentane, 2,3-dimethylbutane, 4-methyl-2-pentene (trans)
8	580	3-Methylpentane
9	600	n-Hexane, 2-ethyl-1-butene
10	620	Methyl cyclopentane, 3-methyl-2-pentene (trans), 2-hexene (cis)
11 <sup>a/</sup>	650	Benzene, 1-methyl cyclopentene
11a <sup>a/</sup>	655	Cyclohexane
12	670	2,3-Dimethylpentane
13	680	Cyclohexene, 3-methylhexane
14	690	2,2,4-Trimethylpentane
15	700	1-Heptene, 3-heptene
16	715	Methyl cyclohexane, 2-heptene (cis)
17	725	2,4-Dimethylhexane, 2,5-dimethylhexane
18	735	2,3,4-Trimethylpentane
19	-	Unknown
20	-	Nitrobenzene

<sup>a/</sup> Peak 11 is the smaller lead shoulder on Peak 11a.



TABLE 6. SCRUBBER WATER ANALYSES

Sample	Date taken	Benzene		Nitrobenzene as benzene		Other organics	
		$\mu\text{g/ml}$	$\text{kg/hr}^{\text{a/}}$	$\mu\text{g/ml}$	$\text{kg/hr}^{\text{a/}}$	$\mu\text{g/ml}$ as benzene	$\text{kg/hr}^{\text{a/}}$
1	September 27	8.7	0.0177	1,400	2.85	110	0.224
2	September 28	1.1	0.0022	360	0.74	90	0.184
3	September 28	1.5	0.0031	475	0.97	85	0.173

a/ Water flow rate of 34  $\ell/\text{min}$  (9 gal/min) used to calculate mass emission rate.

TABLE 7. SAMPLE CONDENSATE ORGANICS ANALYSIS

	Site No. 1 scrubber inlet	Site No. 2 scrubber outlet	Site No. 3 acid receiver
<b>Benzene:</b>			
Total present in condensate (mg) <sup>a/</sup>	10	0.18	0.037
Condensate equivalent vapor concentration (ppm) <sup>a,b/</sup>	16	0.3	0.1
Integrated gas analysis average (ppm) <sup>b/</sup>	425	440	145
Total benzene present in stream (ppm) <sup>a,b/</sup>	441	440	145
<b>Nitrobenzene:</b>			
Total present in condensate (mg) <sup>a/</sup>	11,300	25	375
Condensate equivalent vapor concentration (ppm) <sup>a,b/</sup>	11,680	29	480
Integrated gas analysis average (ppm) <sup>b/</sup>	255	220	280
Total nitrobenzene present in stream (ppm) <sup>a,b/</sup>	11,835	249	760
<b>Total hydrocarbons:</b>			
Total present in condensate (mg) <sup>a/</sup> as benzene)	11,300	46	377
Condensate equivalent vapor concentration (ppm) <sup>a,b/</sup>	11,600	69	482
Integrated gas analysis average (ppm) <sup>b/</sup>	7,300	6,900	3,500
Total hydrocarbons present in stream (ppm) <sup>a,b/</sup>	18,900	6,970	3,980

<sup>a/</sup> Condensate suspected to be primarily entrained liquid.  
Sample was not collected isokinetically.

<sup>b/</sup> Calculated as benzene.

TABLE 8. SUMMARY OF NO<sub>x</sub> RESULTS

Date	Site	Run No.	NO <sub>x</sub> emissions <sup>a/</sup>				
			ppm	lb/dscf	mg/dscm	lb/hr	kg/hr
September 26	No. 1 Organic receiver scrubber inlet	1	35,700	0.00425	68,100	3.53	1.60
			19,200	0.00228	36,500	1.89	0.86
	No. 2 Organic receiver scrubber outlet		4,120	0.00049	7,850	0.41	0.18
			3,450	0.00041	6,570	0.34	0.15
	No. 3 Acid receiver vapor stream		10,800	0.00128	20,500	13.92	6.31
			10,000	0.00119	19,100	12.94	5.88
	No. 1	2	25,200	0.00300	48,100	2.50	1.13
			9,670	0.00115	18,400	0.95	0.43
	No. 2		3,530	0.00042	6,730	0.35	0.16
			3,280	0.00039	6,250	0.32	0.15
September 27	No. 3		8,500	0.00101	16,200	10.98	4.99
			8,330	0.00099	15,900	10.76	4.89
	No. 1	3	27,400	0.00326	52,200	2.71	1.23
			6,390	0.00076	12,200	0.63	0.29
	No. 2		3,450	0.00041	6,570	0.34	0.15
			3,450	0.00041	6,570	0.34	0.15
	No. 3		11,000	0.00131	21,000	14.24	6.47
			5,550	0.00066	10,600	7.18	3.26

<sup>a/</sup> All sample lines contained moisture, possibly nitric acid, so all values may be questionable.

TABLE 9. SUMMARY OF STACK GAS DATA

Site	Stack temp. °F (°C)	Stack gas velocity head in H <sub>2</sub> O (mm H <sub>2</sub> O)	Molecular weight, stack gas	Stack pressure, absolute in Hg (mm Hg)	Mole fraction dry gas	Stack flow rate dscf/min (dscm/min)
No. 1 Organic receiver scrubber inlet	110 <sup>a</sup> / (43)	0.002 (0.051)	28.60	30.13 <sup>a</sup> / (765)	0.914 <sup>b</sup> / (0.914)	13.84 <sup>c</sup> / (0.3918)
No. 2 Organic receiver scrubber outlet	80 <sup>a</sup> / (27)		28.60	30.13 <sup>a</sup> / (765)	0.966 <sup>b</sup> / (0.966)	13.84 <sup>c</sup> / (0.3918)
No. 3 Acid receiver vapor stream	120 <sup>a</sup> / (49)	0.33 (8.41)	28.00	30.13 <sup>a</sup> / (765)	0.899 <sup>b</sup> / (0.899)	181.21 <sup>c</sup> / (5.131)

<sup>a</sup>/ Average of three runs.<sup>b</sup>/ All streams saturated.<sup>c</sup>/ P readings were very low; flow rates have poor accuracy.

A "t" - connector was placed in the integrated bag sampling line (after the condensate trap) and the TGNMO sampling train was connected to this "t." In normal practice the condensate trap used in the sampling line during these tests would not be used for TGNMO sampling; the TGNMO sampling probe would be placed directly into the duct or would be attached (as close to the duct as possible) to any permanent probe tip located in the duct. However, since a primary purpose of these tests was to compare the results of the TGNMO analysis directly with the results of the integrated bag total hydrocarbon (THC) analyses, it was necessary that the two systems sample the same conditioned gas stream.

In general, the TGNMO sampling method consists of pulling a sample from the duct through an organic condensate trap ( $-78^{\circ}\text{C}$ ) into an evacuated tank. The organic contents of the condensate trap and the non-methane organic fraction of the gas sampling tank are analyzed by oxidation to carbon dioxide ( $\text{CO}_2$ ) with subsequent measurement of the  $\text{CO}_2$  by a non-dispersive infrared (NDIR) analyzer; results are expressed as parts per million carbon (ppmc).

Table 10 summarizes the results obtained with the TGNMO method. The test location, run number, sample volume, sample time, volatile organics, condensable organics, and total gaseous non-methane organic concentrations (ppmc) are presented. The volatile organics are those non-methane organics measured in the tank fraction of the sampling train, while the condensable organics are those organics collected in the condensate trap fraction. The total gaseous non-methane concentration is simply the sum of the two sample fractions. The complete laboratory report is included in Appendix D.

During the sampling, a problem was encountered with sample flow blockage. A problem with flow blockage was experienced during runs 1 and 2 at the organic vent scrubber outlet and with run 1 at the waste receiver vent. The problem with flow blockage at the waste receiver vent was probably due to packing the condensate trap too deeply in dry ice; particular care was taken to maintain the proper dry ice level during runs 2 and 3 and no problems were encountered. In an attempt to maintain a constant flow during this test run (Waste Receiver-Run 1), the sample flow control valve was completely opened near the end of the test; this resulted in a situation of initially no sample flow due to blockage followed by an extremely rapid sample flow (half the tank volume in less than 10 min). Apparently, this situation did significantly affect the results for this test run; an abnormally high result was obtained for the tank portion of the sample train (see Table 10). The problem with flow blockage at the organic vent scrubber outlet was probably caused by an excessive amount of moisture in the effluent stream. Both the first and second test runs at this sample location were short due to the blockage problem. The results (see Table 10) for these two test runs (especially run 2) are lower than for the third run, during which no blockage occurred. In order to prevent flow blockage during run 3, a condensate trap maintained at a temperature of  $5^{\circ}\text{C}$  was added to

TABLE 10. SUMMARY OF TGNMO TEST RESULTS

Sample location	Run No.	Date	Sample volume (cc)	Sample time (min)	Volatile organic carbon, ppm C <sub>1</sub>		
					Volatile	Condensable	Nonmethane
Organic vent inlet	1	9/26	3,457	85	1,890	36,300	38,190
	2	9/27	4,082	100	1,470	46,450	47,920
	3	9/28	4,543	105	1,980	21,860	23,840 <sup>a/</sup>
Organic vent outlet	1	9/26	1,171	30	130	18,020	18,150
	2	9/27	1,079	25	330	5,270	5,800
	3	9/28	4,339	105	1,520	30,627 <sup>b/</sup>	32,147
Waste acid receiver	1 <sup>c/</sup>	9/26	4,564	45	20,970	22,190	43,160
	2	9/27	3,506	88	1,830	14,980	16,810
	3	9/28	4,312	105	1,060	16,620	17,680

<sup>a/</sup> Comparison of Post Test Field and Laboratory vacuum readings indicates this tank leaked; therefore, reported results are lower than true value; result calculated on post-test vacuum reading yields 27,390 ppm.

<sup>b/</sup> 3,457 ppm for first condensate trap (5°C); 27,170 for second condensate trap (-78°C).

<sup>c/</sup> Sample rate changed significantly during run; may have affected results.

the sampling train just preceding the condensate trap packed in dry ice. This appears to have alleviated the blockage problem since the third test run was conducted without any abnormal occurrences. The condensable organic value reported in Table 10 for run 3 is the sum of the organic analysis for both traps.

The other anomaly which occurred during these tests was a leak in one of the sample tanks. Upon arrival at the test site, it was noted that two of the evacuated tanks had leaked during shipping. The tank fittings were tightened and both tanks were reevacuated; one tank still had a small leak. Examination of the post-test vacuum readings taken on this tank in the field and in the laboratory indicate the tank leaked during shipping. The organic concentrations value reported by the laboratory is based on the larger sample volume (i.e., actual sample volume plus leakage volume). If the concentration values are recalculated using the sample volume measured in the field, the measured concentrations are 2,317 ppm volatiles, 25,572 ppm condensables, and 27,889 ppm total non-methane organics.

For comparison purposes, Table 11 presents the results obtained by both the TGNMO method and the integrated bag sample method. The total hydrocarbon (THC) values for the integrated bag samples were obtained by directly analyzing the bag sample with a flame ionization detector (FID) calibrated with propane. The results obtained with the FID were multiplied by three (3) to convert the data to a basis of ppm  $C_1$ ; this value is reported in Table 11.

TABLE 11. COMPARISON OF RESULTS FOR TGNMO AND INTEGRATED BAG SAMPLING

Sample location	Run	Volatile organic carbon <sup>a/</sup>		Total hydrocarbon, <sup>b/</sup>
		ppm C <sub>1</sub>	$\frac{a-b}{a}$	ppm C <sub>1</sub>
Organic vent inlet	1	38,190	+27	27,960
	2	47,920	+28	34,200
	3	27,890	+ 8	25,740
Organic vent outlet	1	18,150	-63	29,610
	2	5,800	-308	27,150
	3	32,147	+20	25,740
Waste acid receiver	1	43,160	+73	11,670
	2	16,810	+ 3	16,380
	3	17,680	+21	13,920

<sup>a/</sup> TGNMO method.

<sup>b/</sup> Integrated bag method, flame ionization detection with propane calibration X3.



### SECTION 3

#### PROCESS DESCRIPTION AND OPERATION

The nitrobenzene-aniline production facility at Beaumont was built in 1972 and is a single train of equipment with a nameplate capacity of 145,000 metric tons/year of aniline (all nitrobenzene produced is used to make aniline).

The starting materials, benzene and nitric acid, are reacted in the liquid phase under carefully controlled conditions in the presence of concentrated  $H_2SO_4$ . The resulting crude nitrobenzene and spent acid phases are then separated. The spent acid is extracted with benzene to recover nitrobenzene and then concentrated in a direct contact  $H_2SO_4$  concentrator. Concentrated acid is recycled to the nitration reactor. The benzene extractant also is directed to the nitration reactor. Crude nitrobenzene from the separation step is washed with recycled water and neutralized. The aqueous waste from this step is sent to a wastewater treatment facility. Benzene and water are stripped from the neutralized nitrobenzene stream in a vacuum distillation column. The benzene is recycled to the nitration step, and the purified nitrobenzene is forwarded to intermediate storage to await use in the aniline process. Figure 1 is a simplified flow diagram for the process.

During the sampling runs, the plant was operating stably at a constant rate as determined by monitoring feed rates to the nitration reactors. These rates were as follows:

<u>Date</u>	<u>Annualized aniline equivalent<sup>a/</sup></u> <u>(Mg/yr)</u>
9/26/78	107,100
9/27/78	107,100
9/28/78	53,550

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<sup>a/</sup> Assuming the plant operates 6,833 hr/yr.

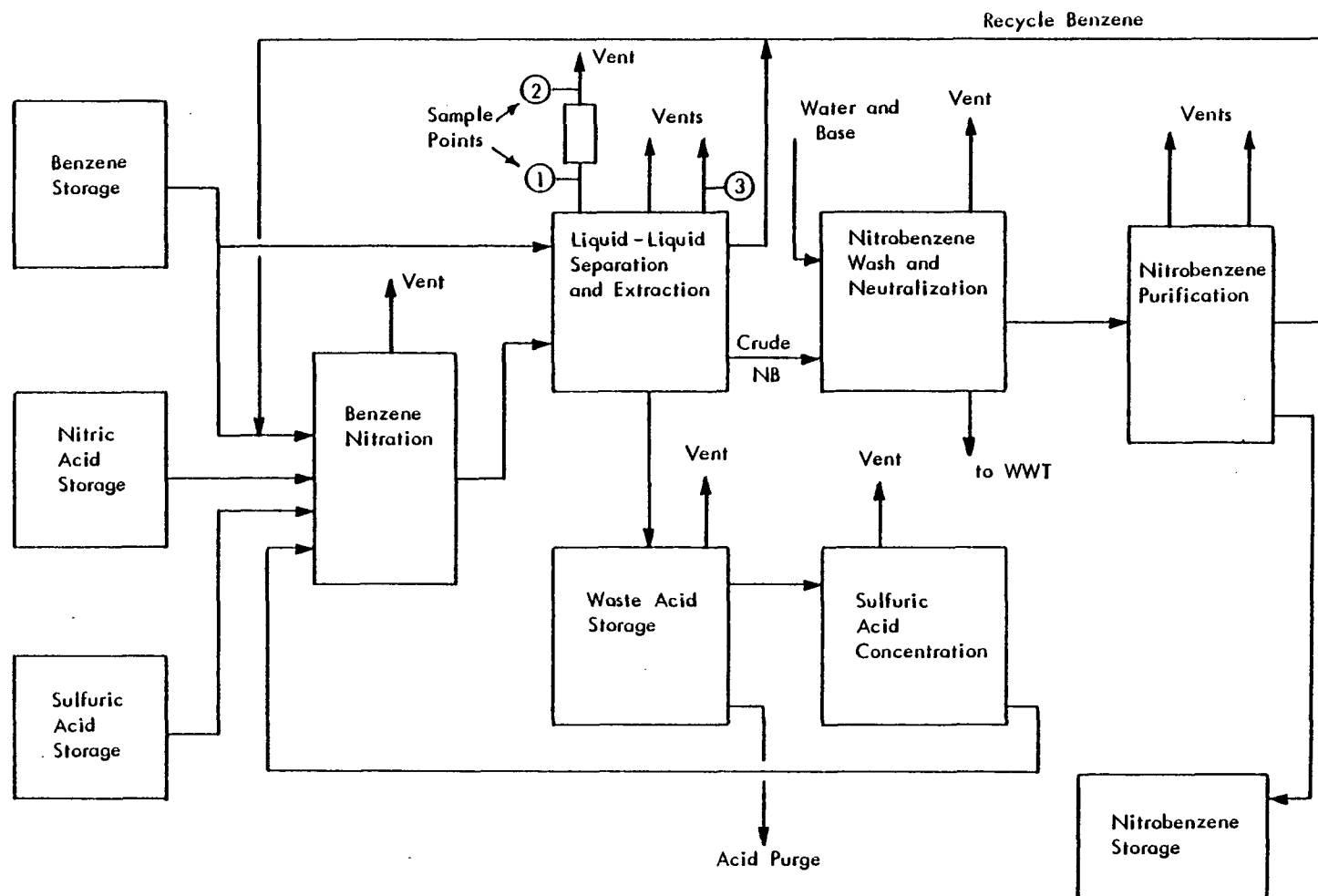


Figure 1. Block diagram of nitrobenzene production.

## SECTION 4

### LOCATION OF SAMPLE POINTS

Figure 2 presents a general site diagram of the sampling location. All of the sample streams were carried to ground level from the respective ducts or sources via stainless steel sample lines.

Figure 3 shows a diagram of sampling site No. 1, the waste organic vapor input stream to the water scrubber. An existing 1.77 cm (0.5 in.) stainless steel sampling line was used. As shown in Figure 2, this line tapped the vapor line approximately 4.3 m (14 ft) above ground level. The "S"-shaped pitot tube was located in the center of the 10.2 cm (4 in.) stainless steel duct approximately 0.6 m (2 ft) above the waste organic receiver. A mercury thermometer was taped to the exterior of the duct at approximately the same location as the pitot tube.

Sampling site No. 2, the vapor output stream from the water scrubber, is shown in Figures 3 and 4. A 0.6 cm (0.25 in.) stainless steel line was run from the top of the scrubber to the ground for sampling purposes. No flow or temperature measurements of the air flow were made at this point. Effluent water samples were taken from the valve in the seal leg, and water flow rates were taken from plant instrumentation.

Figure 5 presents a diagram of sampling site No. 3, the vapor stream off the waste acid receiver. A 0.6 cm (0.25 in.) stainless steel line was again run from the sample tap to ground level for sampling. The "S"-shaped pitot was located in the center of the 5 cm (2 in.) stainless steel duct approximately 1.2 m (4 ft) above the waste acid receiver. A mercury thermometer was used as for the waste organic line for temperature measurements.

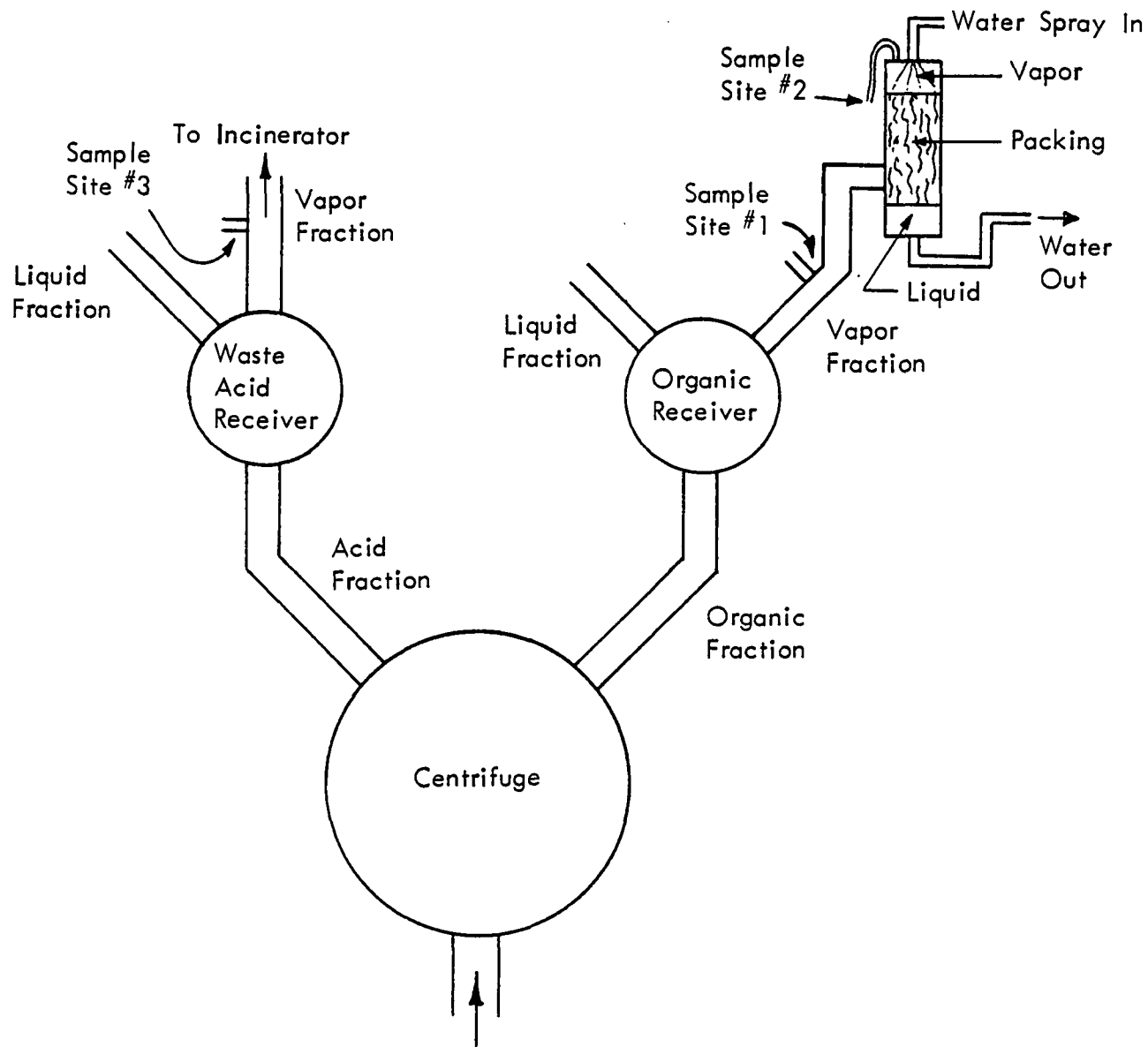


Figure 2. General site diagram - Du Pont/Beaumont.

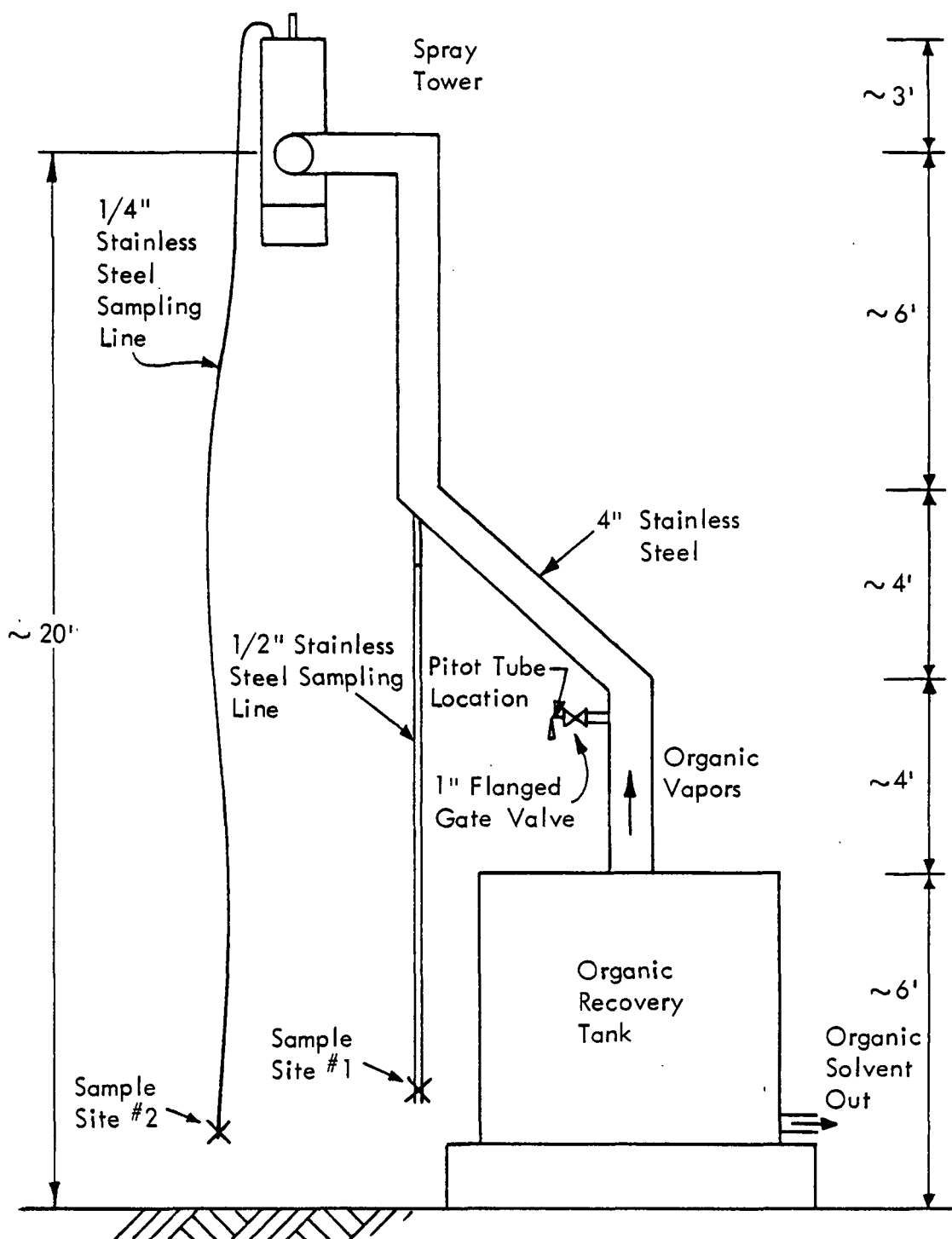


Figure 3. Vapor input stream, water scrubber - site No. 1.

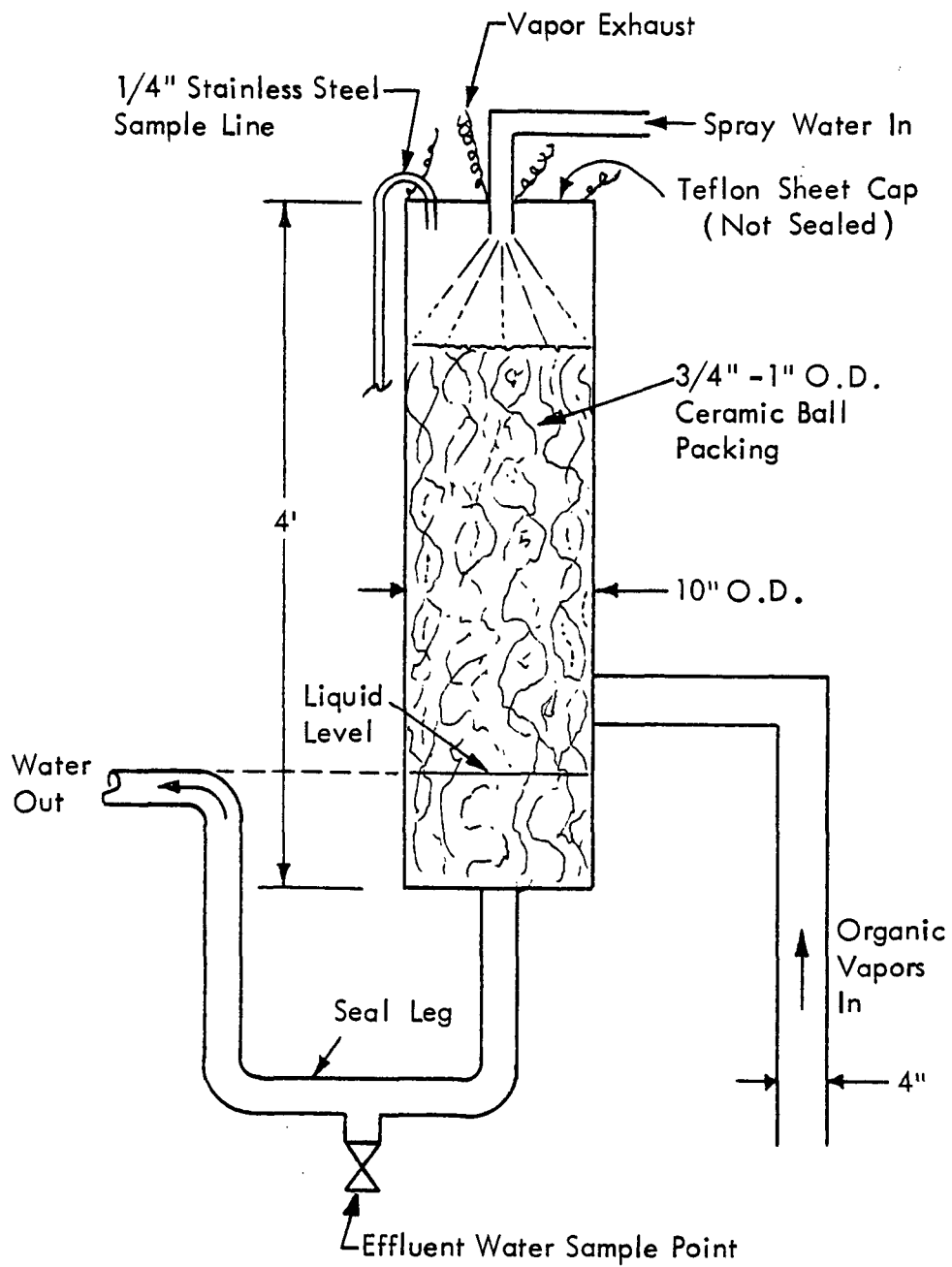


Figure 4. Vapor output stream, water scrubber - site No. 2.

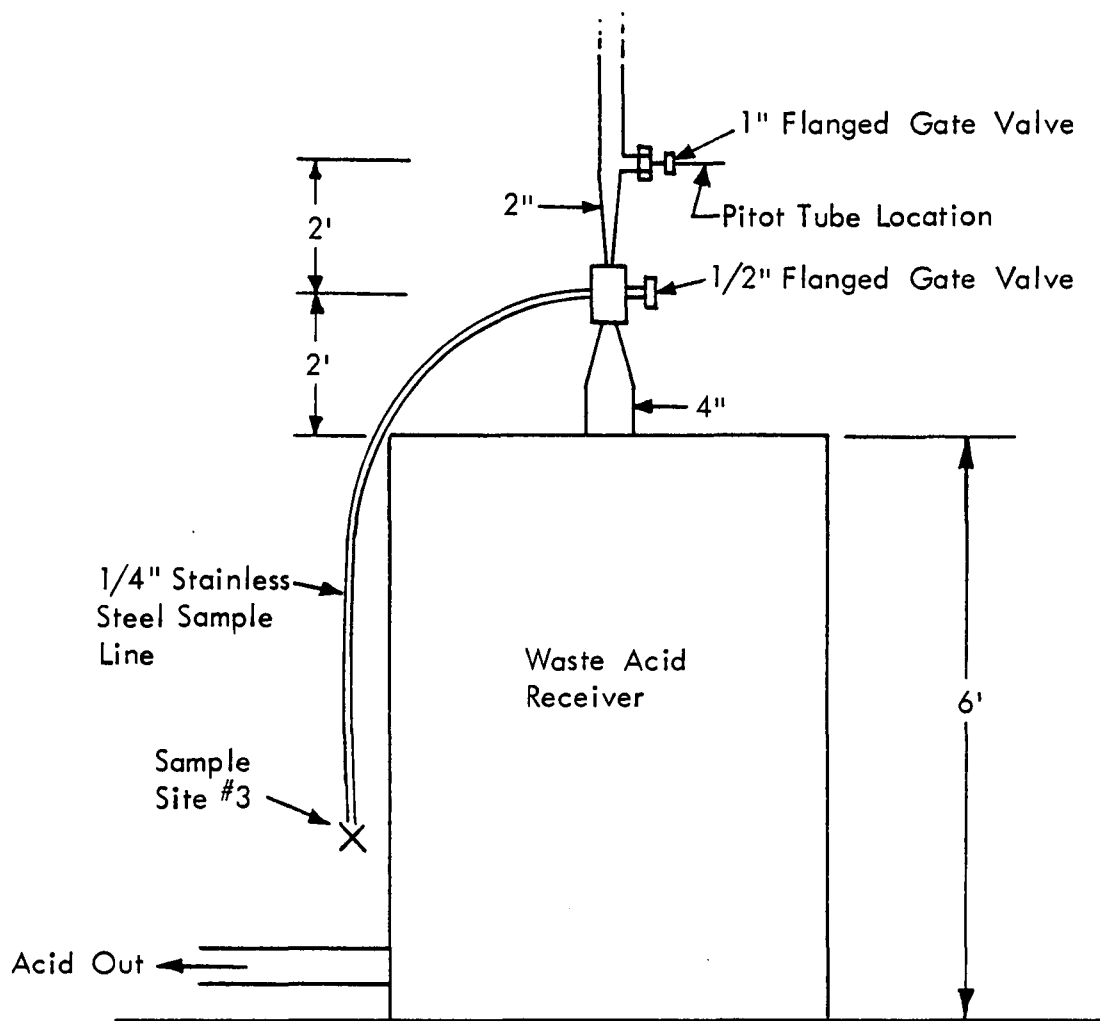


Figure 5. Vapor outlet stream, waste acid tank - site No. 3.

## SECTION 5

### SAMPLING AND ANALYTICAL PROCEDURES

The hydrocarbon samples were obtained according to the September 27, 1977, Environmental Protection Agency (EPA) draft benzene method (Appendix F). Seventy liter aluminized Mylar bags were used with sample times of 1.5 to 2 hr. The sample box and bag were both heated to approximately 49°C (120°F) using copper steam lines and insulation. The sample lines were also insulated and steam heated. Only a short segment of the line just prior to the sample bag was left unheated. A midget glass impinger was fitted into the line ahead of the bag to serve as a condensate knockout trap. This was done to remove as much liquid as possible from the sample stream before the bag. Between the bag and the condensate trap, a "tee" was placed in the line to allow for simultaneous testing by EPA using a different sampling system. Both the sample box and bag were leak-checked prior to each of the three runs. The boxes were transported to the field lab immediately upon completion of sampling. They were heated in the lab using an electric drum heater until all GC analyses had been completed.

Fyrite analysis of the two vapor streams was done for oxygen and carbon dioxide content.

NO<sub>x</sub> samples were obtained from the three sample lines according to EPA Reference Method 7 (Federal Register, Vol. 42, No. 160, August 18, 1977). Two samples per run were obtained following the completion of the hydrocarbon runs. The sample lines were not heated during this testing.

The samples were recovered in the field lab, transferred to shipping bottles, and trucked to MRI for analysis according to Method 7.

Duct velocity measurements were obtained from locations one and three. No significant (0.002 in. H<sub>2</sub>O) flow was ever detected from the waste organic vapor stream (site No. 1). Difficulties were encountered at the waste acid vapor stream (site No. 3) because of the vapor saturation conditions existing in the duct. The pitot lines continually filled with liquid, even when knockout traps were employed. Finally, on the final day, a reverse nitrogen purge was used to clear the lines so that several spot readings could be obtained. Temperature readings from both ducts were obtained by taping and insulating a mercury thermometer to the duct.



All of the organic analyses were performed on a Varian Model 2440 gas chromatograph with flame ionization detector, column bypass valve, and a gas sampling valve with matched, heated 2-cc sample loops. The carbon disulfide extracts were injected by syringe into the injection port. The column used during the field analyses was a 2 m x 1/8 in. OD stainless steel column packed with 3% SP-2100 on 100/120 mesh Supelcoport. A 2 m x 1/8 in. OD nickel column packed with 20% SP-2100/0.1% Carbowax 1500 on 100/120 mesh Supelcoport was used for the compound identification and liquid extract analyses. This mixed phase column gives similar results to the original column but with much less peak tailing and better resolution. Both columns were programmed from 0 to 40° at 4°/min and 40 to 160° at 10°/min (200° limit on the first column).

To measure the benzene concentrations, computer calculations were necessary. Each peak was broken into 3-sec wide segments and the height at each of these segments was measured. These readings were then entered into a BASIC computer program (see Appendix F) which superimposed each sample on the standard peaks and determined the maximum residual for the minor component (benzene). A series of two unknown simultaneous equations were then solved about the points of maximum residual and the peak maximum. The true value of the minor component was the set of solutions having the smallest square of the resulting deviations assuming both peaks have a peak shape identical to the standard peak. The benzene concentrations were then calculated by the ratio of the calculated peak heights to the standard peak height. The standard deviations reported are for the set of solutions obtained for that day's standard peaks (three to six standards). The data resulting from these calculations are reliable within the limits of the standard deviations.

The THC results were obtained with the column bypassed with a short capillary tube and comparing the response against 824 ppm benzene and 2,010 ppm propane standards. The integrated gas samples were compared to the 824 ppm benzene standard.

The condensate samples (composites of all 3 days) and the scrubber water samples were extracted twice with carbon disulfide, and 2  $\mu$ l samples of the disulfide extract were injected into the gas chromatograph. Liquid standards were used for these samples containing 100 and 1,000  $\mu$ /l of benzene and nitrobenzene. Twenty milliliter portions of the scrubber samples and the condensate composite at the scrubber outlet were extracted with two, 5-ml portions of CS<sub>2</sub>. The other composites were extracted entirely with two, 5-ml portions of CS<sub>2</sub>.

Figure 6 is a schematic of the TGNMO sampling train. The TGNMO sampling method is based on the Total Combustion Analysis test procedures established by the Southern California Air Pollution Control District.<sup>1/</sup> During these

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<sup>1/</sup> "Total Combustion Analysis: A Test Method for Measuring Organic Carbon," Salo, Albert E.; Oaks, William L.; MacPhee, Robert D.; Air Pollution Control District - County of Los Angeles, August 1974.

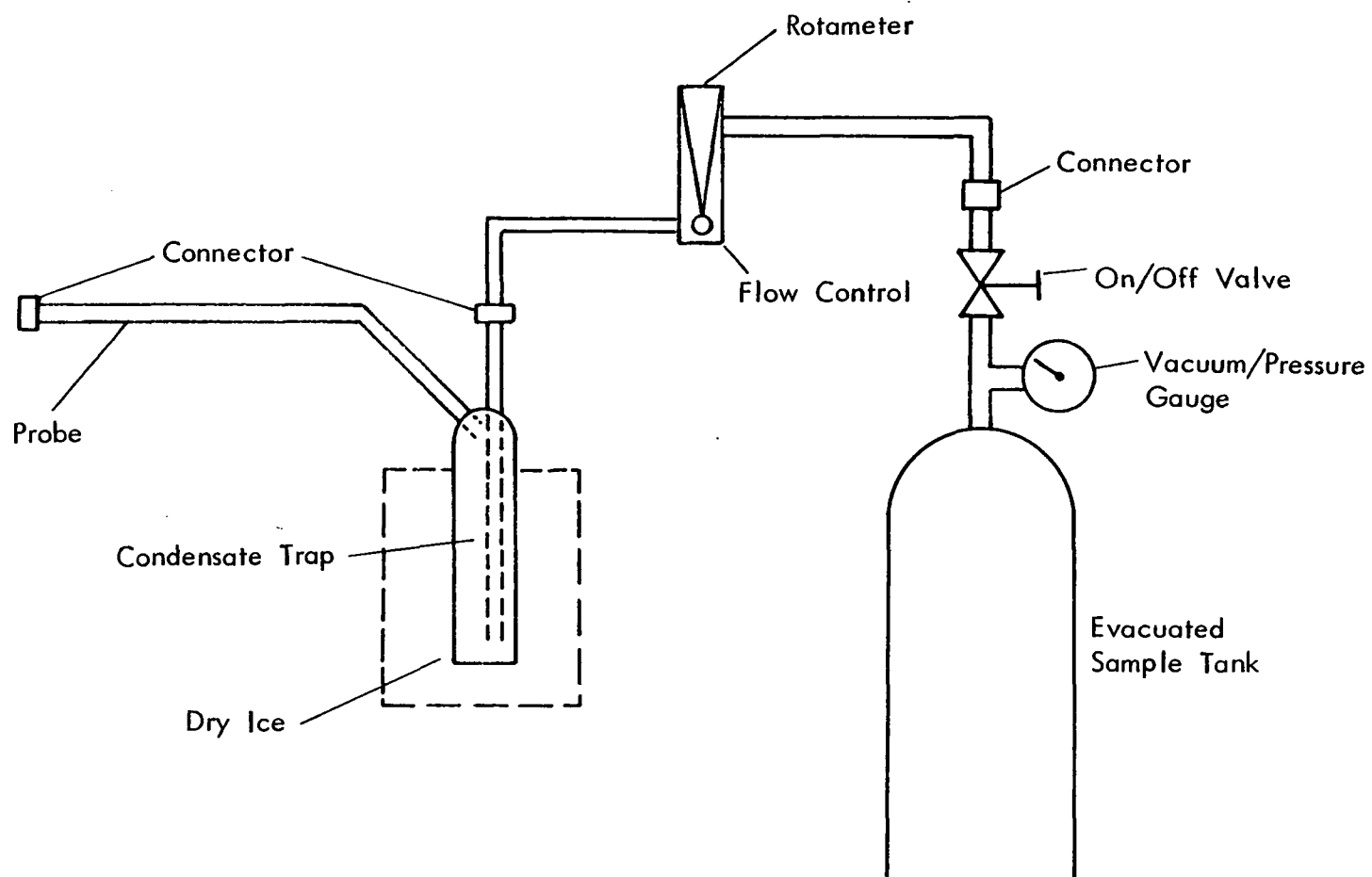


Figure 6. TGNMO sampling train.

tests the sample was drawn from the sample line through a chilled ( $-78^{\circ}\text{C}$ ) stainless steel condensate trap into a 6-liter evacuated aluminum gas collection tank. A rotameter and fine adjust flow control valve were installed between the condensate trap and the evacuated tank to monitor and control the sampling rate. During testing a constant sampling rate of 50 cc/min was maintained. The condensate trap was partially submerged in crushed dry ice during the test and was kept packed in dry ice until analysis. During the last sample run at the organic receiver scrubber outlet, an additional condensate trap was added immediately preceding the regular trap and was kept in a water bath maintained at a temperature of  $5^{\circ}\text{C}$ . This trap was added to the sampling train to prevent sample gas flow blockage caused by freezing of the gas stream moisture in the inlet to the dry ice condensate trap. This problem occurred only at the organic vent scrubber outlet where an excessive amount of moisture was present in the effluent stream.

All sample tanks were evacuated in the laboratory prior to shipment to the field site. The sampling trains were assembled in the field and each train was leak-checked prior to testing. The pretest leak check was conducted by attaching a vacuum pump and manometer (see Figure 7) to the probe tip and then evacuating the sampling train (with the exception of the evacuated tank) to a vacuum of at least 625 mm Hg. After the train was evacuated, the leak check valve 2 was closed and the train was left under vacuum for a 5-min period. Any change in vacuum as measured on the manometer was recorded as the leak rate. A leak rate of less than 0.1 in. mercury for a 5-min period was considered acceptable. The evacuated sample tank assembly was leak-checked prior to assembling the train by simply assuring that the vacuum gauge on the tank did not indicate any change in vacuum in a 1/2-hr period. A post-test leak check was conducted on all sampling trains; in order to perform the post test leak check, the leak check apparatus (with valve 2 closed) was connected to the probe tip. The flow control valve to the tank was then opened until the sampling train reached a constant vacuum; the sample tank flow control valve was closed, and the vacuum measured on the manometer was recorded and monitored for a 5-min period. Any change in the vacuum was recorded as the post-test leak rate.

The analytical work was performed by Truesdail Laboratories, Inc. Total gaseous non-methane organics (TGNMO) were determined by combining the analytical results obtained from independent analyses of the condensate trap and the evacuated tank sample fractions. The organic contents of the condensate trap were oxidized to carbon dioxide ( $\text{CO}_2$ ) which was quantitatively collected and then measured by a non-dispersive infrared (NDIR) analyzer. A fraction of the sample collected in the evacuated tank was injected into a gas chromatograph in order to achieve separation of the non-methane organics from carbon monoxide, carbon dioxide, and methane. Once separated, the four fractions were oxidized to carbon dioxide and separately measured with the NDIR analyzer. The volume of sample collected was calculated from vacuum and pressure readings of the sample tank taken before and after sampling. The measured  $\text{CO}_2$  concentrations and the sample volume were used to calculate the volatile organic carbon concentration of the source effluent as parts per million carbon (ppm  $\text{C}_1$ ).

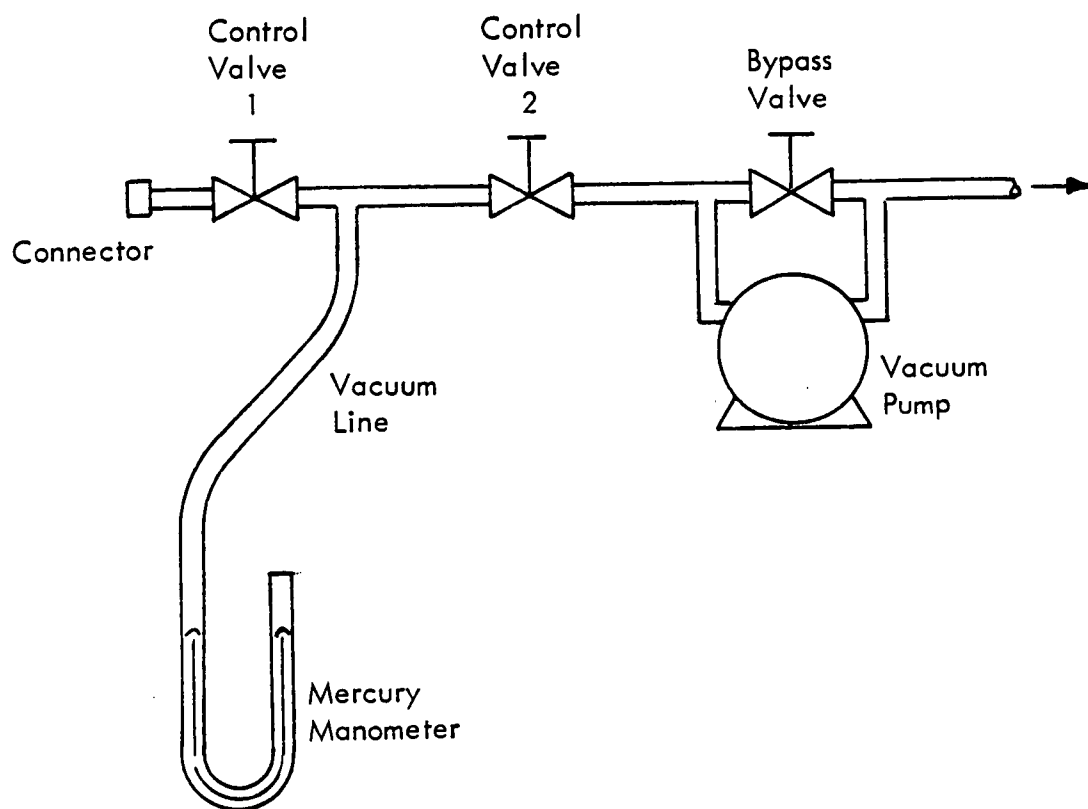


Figure 7. TGNMO sampling train leak check diagram.