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BENZENE SAMPLING PROGRAM  
AT COKE BY-PRODUCT RECOVERY PLANTS:  
WHEELING-PITTSBURGH STEEL CORPORATION  
MONESSEN, PENNSYLVANIA

EPA Contract 68-02-2813  
Work Assignment 48  
ESED Project No. 74/4j

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March 1981

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## 1.0 INTRODUCTION

Scott Environmental Services, a division of Scott Environmental Technology, Inc. conducted a testing program at Wheeling-Pittsburgh Steel Corporation in Monessen, Pennsylvania to determine benzene emissions from the coke by-product recovery plant. The work was performed for the United States Environmental Protection Agency, Emissions Measurement Branch, under Contract No. 68-02-2813, Work Assignment 48. The Monessen plant was the third of seven plants visited to collect data for a possible National Emission Standard for Hazardous Air Pollutants for benzene.

Sampling was conducted at Wheeling-Pittsburgh Steel on August 11-13, 1980. Integrated air samples and liquid samples for benzene analysis were collected from the tar storage tank, light oil storage tank, and the tar intercepting sump.



## 2.0 SUMMARY OF RESULTS

<u>Process</u>	<u>Benzene Emission Rate</u>	
	<u>lb/hr</u>	<u>kg/hr</u>
Tar Storage Tank	0.50	0.23
Light Oil Storage Tank	<1.1	<0.5
Common Tar Intercepting Sump	4.16	1.89



### 3.0 RESULTS AND DISCUSSION

#### 3.1 TAR STORAGE TANK

Tar is stored at approximately 160°F in the #2 tar storage tank to drive off the entrained water and facilitate handling. The tank is vented to the atmosphere, and any benzene in the tar will potentially be released along with the water.

The average emission rate for the tar storage tank is 0.50 lb/hr with a maximum emission rate of 0.85 lb/hr in Run 3, as shown in Table 3-1. Testing was conducted on two consecutive days, and the first day's results are lower than those of the second day. This could be a result of the tank being fuller on the second day of testing; 165,000 gallons as compared to 162,000 gallons.

Also on the first day the stack temperature and velocity were fairly constant during each sampling run whereas during Test 3 on the next day the temperature and flow rate fluctuated considerably. At the end of the test the flow dropped to almost zero, and consequently the temperature dropped to near ambient. This was not caused by any obvious changes such as the sun going behind a cloud, but tank breathing losses are due to many parameters like solar insolation, tank liquid volume, liquid temperature and ambient temperature, and the fluctuations are due to some combination of these variables.

All stack flow rates were corrected to the average conditions at which the benzene concentrations were measured in the Tedlar bags; assumed to be saturated at 68°F and 29.92 inches Hg (2 1/2 % moisture). Example calculations are shown in Appendix A.



TABLE 3-1  
TAR STORAGE DATA SUMMARY

Process		Tar Storage Tank #2		Stack Diameter		8 1/4"			
Plant Wheeling-Pittsburgh Steel, Monessen, PA		Stack Area		0.37 ft <sup>2</sup>					
Run No.	Date	Sample Period	Stack Temp. (°F)	Barometric Pressure (in. Hg)	Stack Velocity (ft/min)	Flow Rate Stack Conditions (ACFM)	Flow Rate Standard Conditions (SCFM)	Benzene Concentration (ppm)	Benzene Emission Rate (lb/hr)
1	8/12/80	1530-1600	95	29.18	60	22	20	1043.1	0.25
2	8/12/80	1710-1740	122	29.18	64	24	19	1658.7	0.39
3	8/13/80	1015-1045	109	29.27	80	30	25	2772.2	0.85
AVG. 0.50									

Standard Conditions: Saturated at 68°F, 29.92 inches Hg

LIQUID SAMPLE DATA

Sample Location	Date	Time	Temp (°F)	Benzene Concentration (ppm by Weight)	Avg.
Flushing Liquor on Surface in Tank	8/13/80	1520	168	1580	1606
				1672	
				1565	
Inlet to Tar Tank - From Pump	8/13/80	1455	160	1765	1867
				2159	
				1677	



Liquid temperatures were 71°C at the inlet and 75.5°C in the tank. The liquid surface samples contained mainly flushing liquor, which forms the upper phase in the tank over the tar layer. The surface layer samples contained 1600 ppm benzene, and the tar collected from the inlet pump had 1870 ppm benzene.

### 3.2 LIGHT OIL STORAGE TANK

The #7 light oil storage tank holds a mixture of the light and heavy fractions from the rectifier. The liquid contains approximately 70% benzene by weight and is stored at ambient temperature. The tank is vented to the atmosphere and is thus a potential benzene emission source. At the time of sampling the only tank emissions were due to tank breathing losses.

The light oil storage tank had an average emission rate of less than 1.1 lb/hr. This tank had a very high concentration of benzene in the headspace but no outflow was detectable with the anemometer. Emission rates from the tank are based on the flow rate being less than the lowest detectable limit of the anemometer, which is 12 feet per minute.

The high benzene concentration in the vapor (~2.5%) is due to the high percentage of benzene in the light oil (70%). However, at ambient temperature the vaporization rate of the light oil was too slow to drive a measureable flow velocity from the vent.



TABLE 3-2  
LIGHT OIL STORAGE DATA SUMMARY

Run No.	Date	Sample Period	Stack Temp. (°F)	Barometric Pressure (in. Hg)	Stack Velocity (ft/min)	Flow Rate Stack Conditions (ACFM)	Flow Rate Standard Conditions (SCFM)	Benzene Concentration (ppm)	Benzene Emission Rate (lb/hr)
1	8/12/80	1532-1602	93	29.18	*	<4	<4	29500	<1.2
2	8/12/80	1645-1715	93	29.18	*	<4	<4	22900	<0.9
3	8/13/80	1022-1052	77	29.27	*	<4	<4	25400	<1.1
									AVG. <1.1

\*Not Detectable - less than 12 fpm  
Standard Conditions: Saturated at 68°F, 29.92 inches Hg

LIQUID SAMPLE DATA

Sample Location	Date	Time	Temp (°F)	Benzene Concentration (ppm)
Light Oil Outlet - From Pump	8/13/80	1505	77	680,000
				750,000
				670,000
				AVG. 700,000 (70%)



### 3.3 TAR INTERCEPTING SUMP

The common tar sump receives ammonia liquor, tar from the primary cooler, tar from the crude tar storage tanks, pump room floor drain wastewater, exhauster booster and seal pump wastewater, Cottrell precipitator wastewater, and condensate from the desuper heater. A pump then feeds the material directly to the decanters. The sump is approximately 4' x 8' and is open to the atmosphere, constituting a potential fugitive benzene emission source.

The benzene emission rates varied from 2.99 to 4.91 lb/hr with an average of 4.16 lb/hr. The data collected at this source exhibits an effect not observed at any other source tested using the tracer gas method. The concentrations of benzene and isobutane vary as much as 95% between sampling locations on the same run but the mass to mass ratios were in close agreement. The variable wind at this location undoubtedly accounts for this effect.

The liquid samples collected at the sump had a temperature of about 150°F and contained approximately 1700 ppm benzene in the tar fraction and 2400 ppm benzene in the top fraction, which was mainly flushing liquor.



TABLE 3-3

## TAR INTERCEPTING SUMP

Date: 8/12/80  
 Test #1, Run #1  
 Test Start - 11:25 a.m.

Isobutane Release Rate: 0.872 lb/hr  
 0.396 kg/hr

Sample Loc.	Conc. of Benzene (ppm)	Conc. of Isobutane (ppm)	Mass to Mass Ratio $\phi/ic_4$	lb/hr Benzene	kg/hr Benzene
West 1	5.78	2.23	3.48	3.03	1.38
West 2	1.28	0.26	6.52	5.69	2.59
North 1	3.95	1.56	3.39	2.96	1.35
North 2	13.14	2.30	7.67	6.69	3.04
Upwind	0.56	0.30			
				Avg. 4.59	Avg. 2.09

Date: 8/12/80  
 Test #1, Run #2  
 Test Start - 2:22 p.m.

Isobutane Release Rate: 1.121 lb/hr  
 0.508 kg/hr

West 1	4.56	1.84	3.33	3.73	1.70
West 2	1.43	0.50	3.80	4.26	1.94
North 1	9.33	4.14	3.03	3.40	1.55
North 2	-19.72	8.65	3.07	3.44	1.56
Upwind	0.34	0.10			
				Avg. 3.71	Avg. 1.67
				Average Emission 4.15	1.89

Date: 8/13/80  
 Test #2, Run #1  
 Test Start - 8:35 a.m.

Isobutane Release Rate: 1.145 lb/hr  
 0.519 kg/hr

West 1	8.09	2.92	3.72	4.26	1.94
West 2	4.73	1.52	4.18	4.79	2.18
North 1	14.20	3.89	4.91	5.62	2.55
North 2	3.41	1.06	4.33	4.96	2.25
Upwind	2.86	1.00			
				Avg. 4.91	Avg. 2.23



Table 3-3  
(Continued)

Date: 8/13/80  
 Test #2, Run #2  
 Test Start - 11:25 a.m.

Isobutane Release Rate: 1.122 lb/hr  
 0.509 kg/hr

Sample Loc.	Conc. of Benzene (ppm)	Conc. of Isobutane (ppm)	Mass to Mass Ratio $\phi/ic_4$	lb/hr Benzene	kg/hr Benzene
West 1	8.48	2.88	3.97	4.45	2.02
West 2	4.66	1.54	4.07	4.57	2.07
North 1	10.18	3.70	3.70	4.15	1.89
North 2	17.17	4.78	4.83	5.42	2.46
Upwind	0.42	0.10			
				Avg. 4.65	Avg. 2.11
				Average Emission 4.78	2.17

Date: 8/13/80  
 Test #3, Run #1  
 Test Start - 1:23 p.m.

Isobutane Release Rate: 1.176 lb/hr  
 0.533 kg/hr

West 1	6.15	2.85	2.90	3.41	1.55
West 2	2.07	1.01	2.75	3.23	1.47
North 1	6.36	3.08	2.06	2.42	1.10
North 2	11.24	6.16	2.45	2.88	1.31
Upwind	0.34	ND			
				Avg. 2.99	Avg. 1.36

Date: 8/13/80  
 Test #3, Run #2  
 Test Start - 2:07 p.m.

Isobutane Release Rate: 1.216 lb/hr  
 0.552 kg/hr

West 1	5.30	2.09	3.41	4.15	1.89
West 2	2.26	0.85	3.57	4.43	1.97
North 1	9.75	4.00	3.28	3.99	1.81
North 2	16.11	6.90	3.14	3.82	1.74
Upwind	0.58	0.14			
				Avg. 4.08	Avg. 1.85
				Average Emission 3.54	1.61



TABLE 3-4

## LIQUID SAMPLE DATA: COMMON TAR SUMP

Date: 8/13/80

Time: 1345

Sample Temp.: 150°F

<u>Sample Fraction</u>	<u>Benzene Concentration (ppm by Weight)</u>	
Heavy Fraction - Sample 1	1740	
Sample 2	2020	Avg. 1720
Sample 3	1400	
Light Fraction - Sample 1	4.0	
Sample 2	1.03	Avg. 3.78
Sample 3	6.3	

NOTE: Triplicate liquid samples were dipped from the sump. Each sample was separated into heavy and light fractions and each fraction was analyzed separately.



#### 4.0 PROCESS DESCRIPTION

The Wheeling-Pittsburgh Steel Corporation coke plant at Monessen, Pennsylvania started construction in 1942. Approximately 90 percent of the coke plant, including by-product recovery operations, was constructed in 1942 using a Koppers design. The processes used at the Monessen plant for recovery of coke oven gas are primary cooling, tar decanting, turbine exhausting, tar electrostatic precipitation (ESP), Koppers semi-direct ammonia absorption, ammonia still, tar bottom final cooling, light oil recovery, and clean coke oven gas reuse. A process flow diagram of the gas and liquid streams is depicted in Figure 4-1.

The gas leaving the ovens is collected in collecting mains where it is sprayed with flushing liquor for initial cooling. The gas and the flushing liquor leave the battery area and are transported from the collecting main through a crossover main into the suction main and then into the by-product recovery area. The gas and liquid initially separate in the by-product recovery area at a downcomer where the flushing liquor falls out and is discharged to the tar decanter, while the gas continues to the primary coolers.

The two tar decanters in parallel separate the liquor into tar and flushing liquor layers. Additional inputs to the tar decanters come from the common tar intercepting sump and the final cooler. The flushing liquor is pumped to the flushing liquor running tank before returning to the battery spray system. The excess flushing liquor is pumped to a holding tank before processing in an ammonia still where caustic is added to the



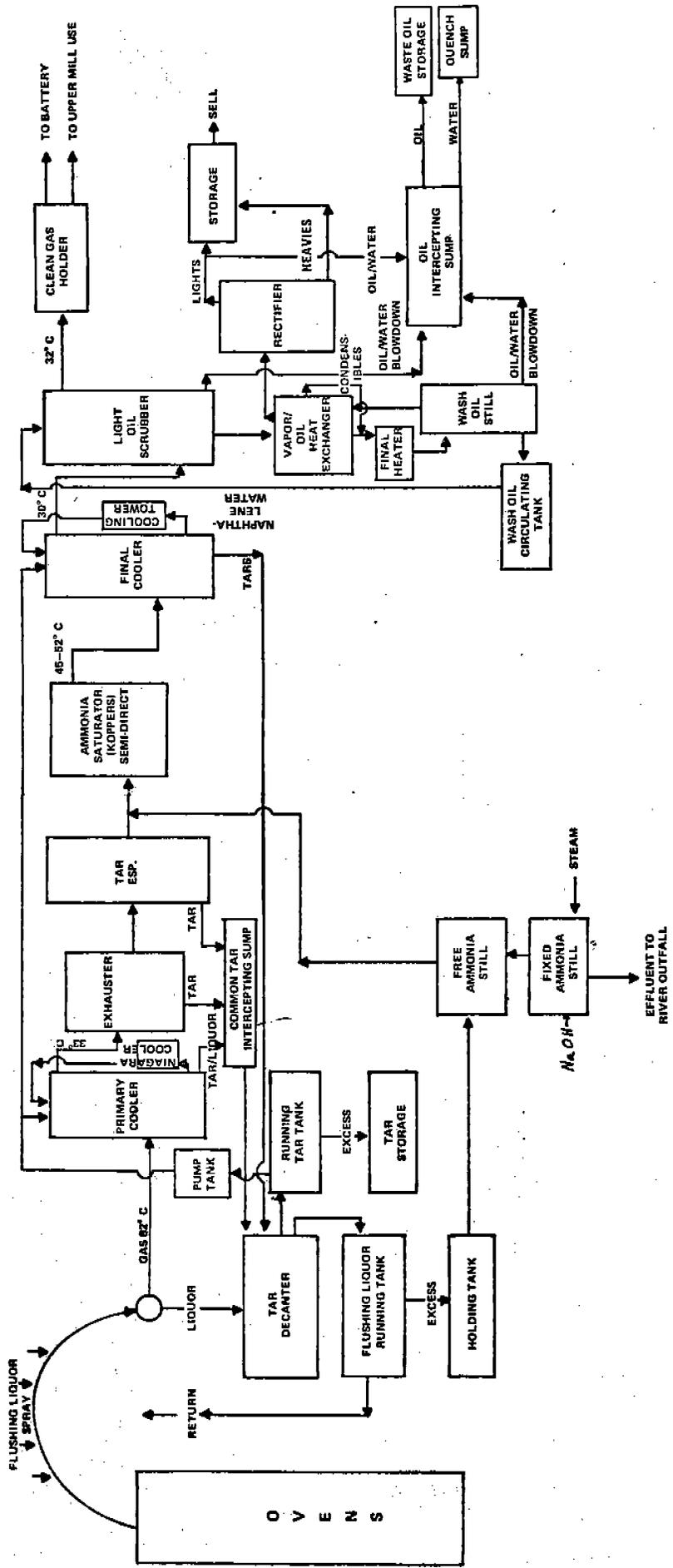


Figure 4-1

liquor. The tar layer is pumped to an 18 cubic meter (4,000 gallon) running tar tank before pumping to a pump tank. Excess tar from the running tar tank is pumped to three of the four tar storage tanks. The tar from the pump tank is circulated to the primary cooler and the final cooler. The tar flow to both units varies proportionally with the naphthalene concentration.

The gas stream from the downcomer enters the direct primary coolers at approximately 82°C. There are three parallel primary coolers at the plant, but only two were on-line during the visit. The circulating liquor is cooled by indirect Niagara coolers that circulate river water which is atmospherically cooled. Excess tar and liquor are discharged to the common tar intercepting sump.

The gas exits the primary coolers at approximately 30°C and enters the turbine exhausters. There are two turbine exhausters, but only one was in operation at the time. The gas stream in the exhauster changes from vacuum to positive pressure which supplies the motive power for the system. Some tars are separated in the exhauster and drained to the common tar intercepting sump.

The gas enters the tar ESP where additional tar is separated from the gas and drained to the common tar intercepting sump. There are three parallel ESP's and all were in operation during the plant visit. The plant can operate on only one tar ESP. However, normal operation is two and the preference is three.

The gas stream from the tar ESP's is combined with the ammonia vapor from the ammonia still and enters the ammonia saturator. There are two Koppers semi-direct ammonia saturators used one at a time. The gas



stream is contacted with sulfuric acid which produces ammonium sulfate crystals as the final product. The gas leaves the ammonia recovery operation at approximately 45-52°C.

The gas then enters the final cooler. There are two final coolers also used one at a time. The final coolers are tar bottom coolers that circulate water and tar. The naphthalene-lean water is cooled in an atmospheric cooling tower and the naphthalene-rich tar is pumped to the tar decanter for separation. Tar is continuously recirculated to the final cooler. The rate of circulation is determined by withdrawal of samples through a manifold system on the side of the cooler.

The gas leaves the final cooler at approximately 30°C and enters the light oil scrubbers. There are two light oil scrubbers in series with countercurrent flow of the wash oil and the gas stream. The benzolized wash oil leaves the bottom of the light oil scrubber and passes through a vapor/oil heat exchanger before entering the final heater. After the final heater, the benzolized wash oil enters the wash oil still where the light oil is steam-stripped from the wash oil. The light oil vapors leave the top of the still and pass through the vapor/oil heat exchanger before entering the rectifier. The debenzolized wash oil is pumped to the wash oil circulating tank before recirculating to the light oil scrubbers. Oil/water blowdown from the light oil scrubbers, the wash oil still, and the rectifier is drained to the oil intercepting sump. After the rectifier, the light and heavy fractions are combined in final storage.



The clean gas exits the light oil scrubbers at approximately 32°C and enters the gas holder before boosting to the battery underfire and upper mill use. The clean coke oven gas has a heating value of 580-527kJ (550-530 Btu) and is not mixed with natural gas to increase this value.

#### 4.1 PROCESS OPERATING PARAMETERS

During the tests, the coke output of the plant was 524 tons per day. Battery 1A, with 37 ovens (6 ovens not operating), and Battery 2, with 19 ovens, were operating. The coking time was 24 hours for Battery 1A and 22.5 hours for Battery 2. The amount of coke oven gas produced was 8 to 8.5 million cubic feet per day. The coal blend was 35 percent high volatile coal (1.42 to 1.48 percent sulfur), 48 percent of a different type high volatile coal (0.68 to 0.74 percent sulfur), and 17 percent low volatile coal. The coal make-up was 17 percent low volatile coal and 83 percent high volatile coal for Battery 1A and 12 percent low volatile coal and 88 percent high volatile coal for Battery 2.

Table 4-1 contains the storage tank process data recorded during the emission tests. Light oil and crude tar production rates during the tests were approximately 2,500 gallons per day and 6,000 gallons per day, respectively. Approximately 13,000 gallons of light oil were shipped from storage on both test days. Crude tar is shipped once a month. The light oil and crude tar tank capacities are 125,000 gallons and 250,000 gallons, respectively.

The common tar intercepting sump contains ammonia liquor, tar from the primary cooler, tar from the crude tar storage tanks, pump room floor drain wastewater, exhaust booster and seal pump wastewater,



Cottrell precipitator wastewater, and condensate from the desuper heater. The liquid level in the sump was approximately 2 feet below the level recorded in the presurvey. Plant personnel confirmed that the low level of liquid in the sump was caused by decreased plant production. The liquid in the sump during the emission tests was approximately 0.83 feet deep. The liquid temperature in the sump during the emission tests was approximately 19°C.



TABLE 4-1 STORAGE TANK PROCESS DATA

<u>Unit</u>	<u>Test Run</u>	<u>Test Date</u>	<u>Tank Interior Temperature (°C)</u>	<u>Tank Liquid Volume (gallons)</u>
Number 7 Light Oil Storage Tank	1	8/12/80	30	31,000
	2	8/12/80	30	31,000
	3	8/13/80	30	26,000
Number 2 Crude Tar Storage Tank	1	8/12/80	65	162,000
	2	8/12/80	65	162,000
	3	8/13/80	65	165,000



## 5.0 FIELD SAMPLING AND ANALYSIS METHODOLOGY

### 5.1 DETERMINATION OF BENZENE FROM STATIONARY SOURCES: EPA METHOD 110 AND MODIFICATIONS

EPA Method 110 consists of drawing a time-integrated stack gas sample through a probe into a Tedlar\* sample bag, which is enclosed in a leak-free drum, by use of a pump hooked to the drum outlet which slowly evacuates the drum, causing the bag to fill. A copy of the method is included in Appendix D.

The method was modified by Scott because as it stands the method doesn't account for moisture in the sample stream, and is only designed to measure benzene concentration, not mass emission rate. The following modifications were made to all tests done using Method 110:

1. To obtain mass emission rates, velocity and temperature readings were taken at the top of the stack at 5 minute intervals during the 30-minute sampling runs. This information was used to calculate flow-rate, which was used in conjunction with the benzene concentration to yield the mass emission rate. Velocity readings were made using a vane anemometer with direct electronic readout.

2. A personnel sampling pump was substituted for the pump, needle valve, and flowmeter of the method. The personnel pumps have built-in flowmeters and rate adjustment screws and have the further advantage of being intrinsically safe, as required in many areas of the coke plant.

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\* Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.



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3. Swagelok fittings were used in place of quick-connects.
4. Rather than discarding Teflon sample lines after each set of samples, they were washed with propylene carbonate and/or acetone and flushed with nitrogen before reuse.
5. An orifice and magnehelic gauge were inserted in the sampling line before the Tedlar bag to indicate that air flow was reaching the bag.
6. A water knockout trap was inserted between the probe and magnehelic gauge to collect any condensate in the sample line.
7. The following cleanup procedures were followed:

If any condensate was collected in the trap or sample line, it was measured and saved for analysis. The probe, line and trap were then washed with propylene carbonate, which was also saved for analysis. Any benzene found in these washes and water catches was added to the total found in the sample bag to determine mass emission rates.

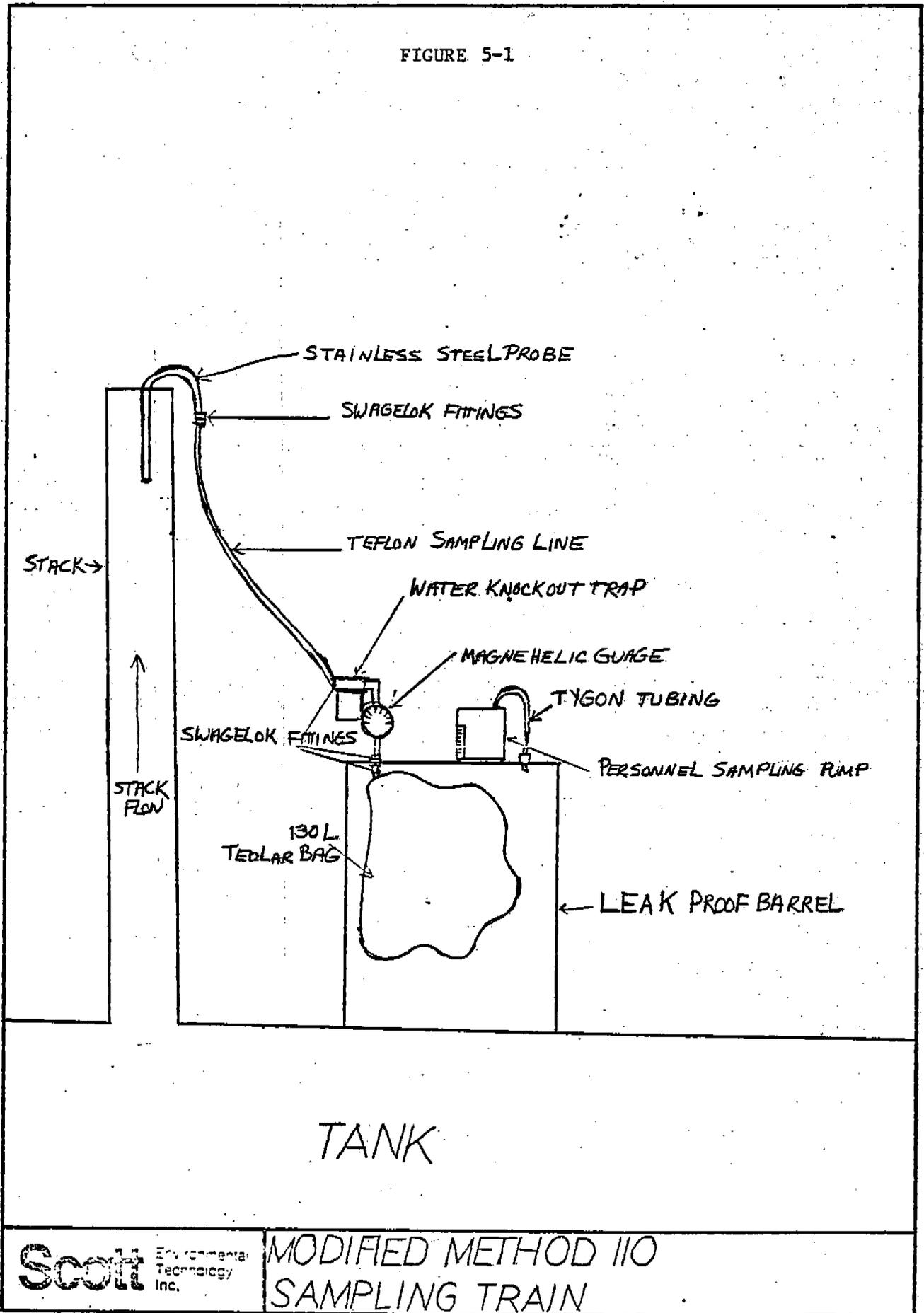
Bag volumes were measured whenever water was collected in the trap by emptying the bag through a dry gas meter after the sample was analyzed. The volume of water collected in the trap was then converted to an equivalent air volume and was added to the volume in the bag to determine the percent moisture in the sample stream.

After the probe, line and trap washes were completed, the lines were washed with acetone to remove the propylene carbonate film and flushed with nitrogen to dry.

Figure 5-1 shows the modified Method 110 setup.



FIGURE 5-1



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MODIFIED METHOD 110  
SAMPLING TRAIN

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## 5.2 TRACER TESTING

The tracer gas method is a practical procedure for quantifying mass emissions of volatile organics from sources which are essentially open to the atmosphere without disturbing flow, dispersion patterns or the source operation. This method utilizes the release of a tracer gas directly over the source of interest; the tracer gas will then follow the same dispersion patterns as the emissions from the source. The mass of tracer released over the sampling period is known and the mass to mass ratio of the benzene to the tracer gas in the sample is determined by gas chromatography. The emission rate of benzene can be calculated with this information.

This method is based on the principle that the chosen tracer gas will model the dispersion of benzene from the source. The tracer gas chosen for this project was isobutane because it was not present in the sources to be tested and it could readily be separated from other source trace components by the same column used for benzene. In addition, isobutane is a non-toxic gas that can readily be dispensed from a pressurized cylinder at a uniform measured rate.

When this method was used triplicate tests were performed. Each test consisted of two 1/2 hour runs. For each run clean and backgrounded ten-liter Tedlar bags were used. Integrated samples were collected using Emission Measurements, Inc. Air Quality Sampler II systems. The AQS II samplers are self-contained units capable of collecting one or more integrated samples at a preset rate. For tracer tests the sampling rate used was ten liters per hour.

## 5.3 SAMPLE HANDLING

After being collected the gas samples were immediately transported to the gas chromatograph and analyzed. The elapsed time between sample collection and analysis never exceeded one hour. To verify that there was no sample degradation in samples of this type some of the samples were retained for 24 hours and reanalyzed. The loss of benzene and isobutane observed was typically less than 5%.



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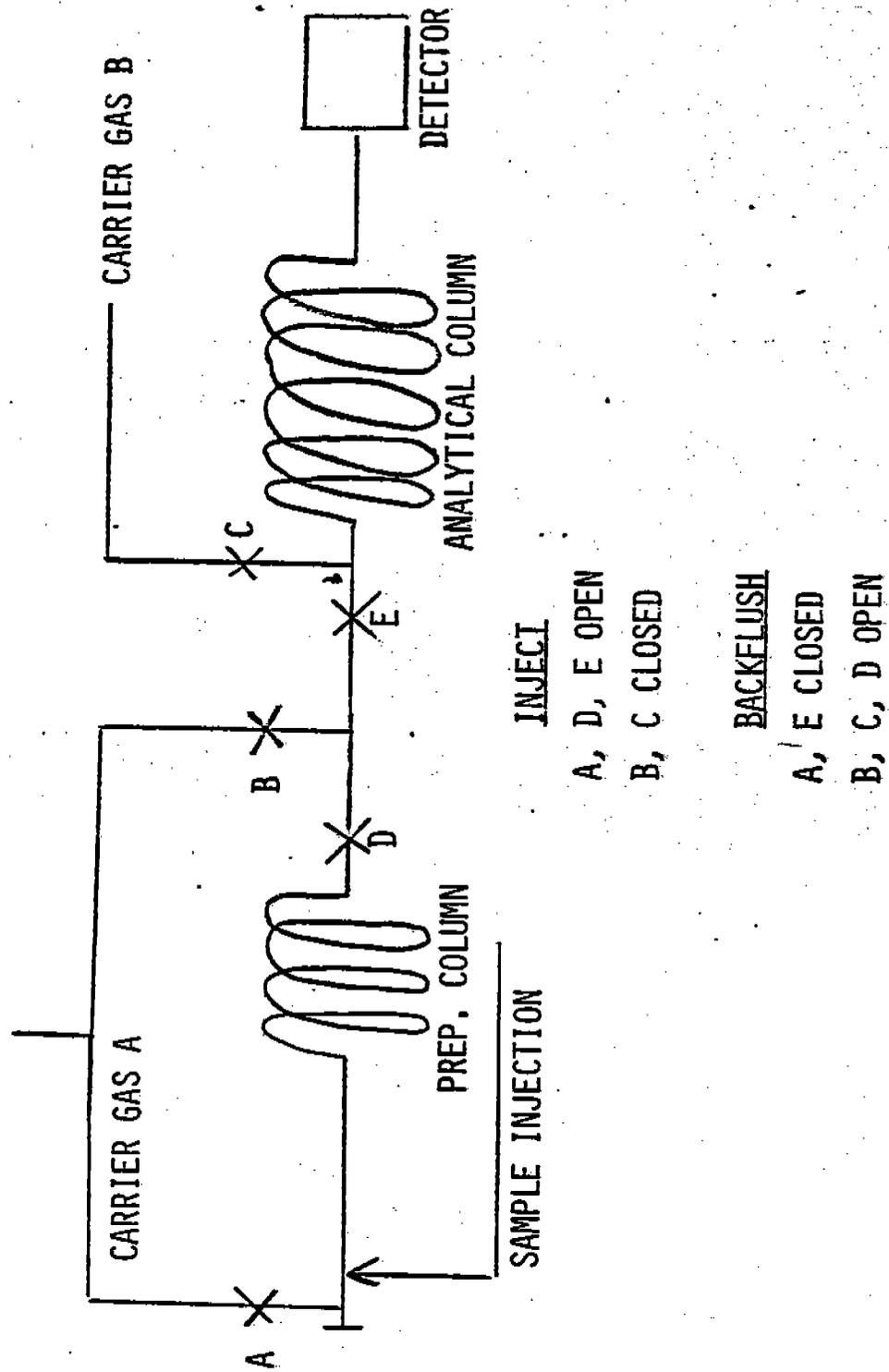
#### 5.4 FIELD ANALYSIS

All gas samples collected were analyzed using a Shimadzu GC Mini 1 gas chromatograph equipped with dual flame ionization detectors, dual electrometers, heated sample loop and a backflush system. Figure 5-2 shows a schematic of the backflush apparatus. The backflush system is composed of ten port sequence reversal valve and two columns, a scrubber column for retaining high molecular weight compounds and an analytical column. When the system is in the inject mode the scrubber column and the analytical column are connected in series allowing sample components to move from the precolumn to the analytical column. In the backflush mode the columns are disconnected from each other and become two separate systems each with its own carrier gas source. This arrangement allows the separation and measurement of low molecular weight compounds while the scrubber column is being backflushed of heavier sample components. Backflush times for different mixtures of sample components must be predetermined to insure that the compound(s) of interest are transferred to the analytical column before backflushing is started.

Samples for chromatographic analysis were drawn into a 20 cc glass syringe then introduced to the sample loop inlet. The samples once in the sample loop were allowed to come to atmospheric pressure by waiting 15 seconds prior to the injection. When only benzene was of interest the following chromatographic conditions were maintained:

Column Temperature (isothermal)	- 100°C
Injector and Detector Temperature	- 200°C
5 ml Sample Loop, Temperature	- 50°C
Carrier Gas Flow Rate	- 32 cc/min
Hydrogen Flow Rate	- 40 cc/min.
Air Flow Rate	- 240 cc/min.
Analysis Time	- 5 min.
Detector	- Flame Ionization





GC COLUMN CONFIGURATION WITH BACKFLUSH

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The columns used for field analysis were:

A - Scrubber Column

10% FFAP on Supelcoport 80/100  
1/8" x 1 m Stainless Steel

B - Analytical column

20% SP-2100, 0.1% Carbowax 1500  
100/120 Supelcoport  
1/8" x 10' Stainless Steel

When samples from tracer tests were analyzed the chromatographic conditions were changed to provide adequate separation of the isobutane tracer from the other light components of the sample. The temperature program used for this analysis was:

- 1) Start at room temperature with external cooling fan on and oven door open.
- 2) Inject @ 0.0 min.
- 3) Turn external cooling fan off @ 1.0 min.
- 4) Backflush @ 1.8 min.
- 5) Isobutane elutes @ 2.3 min.
- 6) Close oven door @ 3.0 min. with oven temperature set at 100°C.
- 7) Benzene elutes @ 7.0 min.
- 8) After the elution of benzene, open the oven door and turn on the cooling fan. The next injection can be made after 2 minutes of cooling.
- 9) When the tracer gas is used analysis time will be approximately 10 minutes.

The columns and flow rates were the same as for isothermal.



## 6.0 FIELD SAMPLING PROCEDURES

### 6.1 TAR STORAGE TANK

Three half-hour EPA Method 110 tests were conducted on the tar storage tank on August 12th and 13th, 1980.

Before beginning, the naphthalene that had accumulated around the test vent was knocked away to insure accurate velocity readings, and the manway, which was found open, was covered. The runs all were very straightforward and no problems were encountered. The tests were run concurrently with the light oil storage tank runs, as the tanks were adjacent to one another and connected by a walkway across the top (See Figure 6-1).

Liquid samples were collected from the inlet to the tank via a pump at ground level, and from the surface of the liquid in the tank by dipping with a bucket on a line.

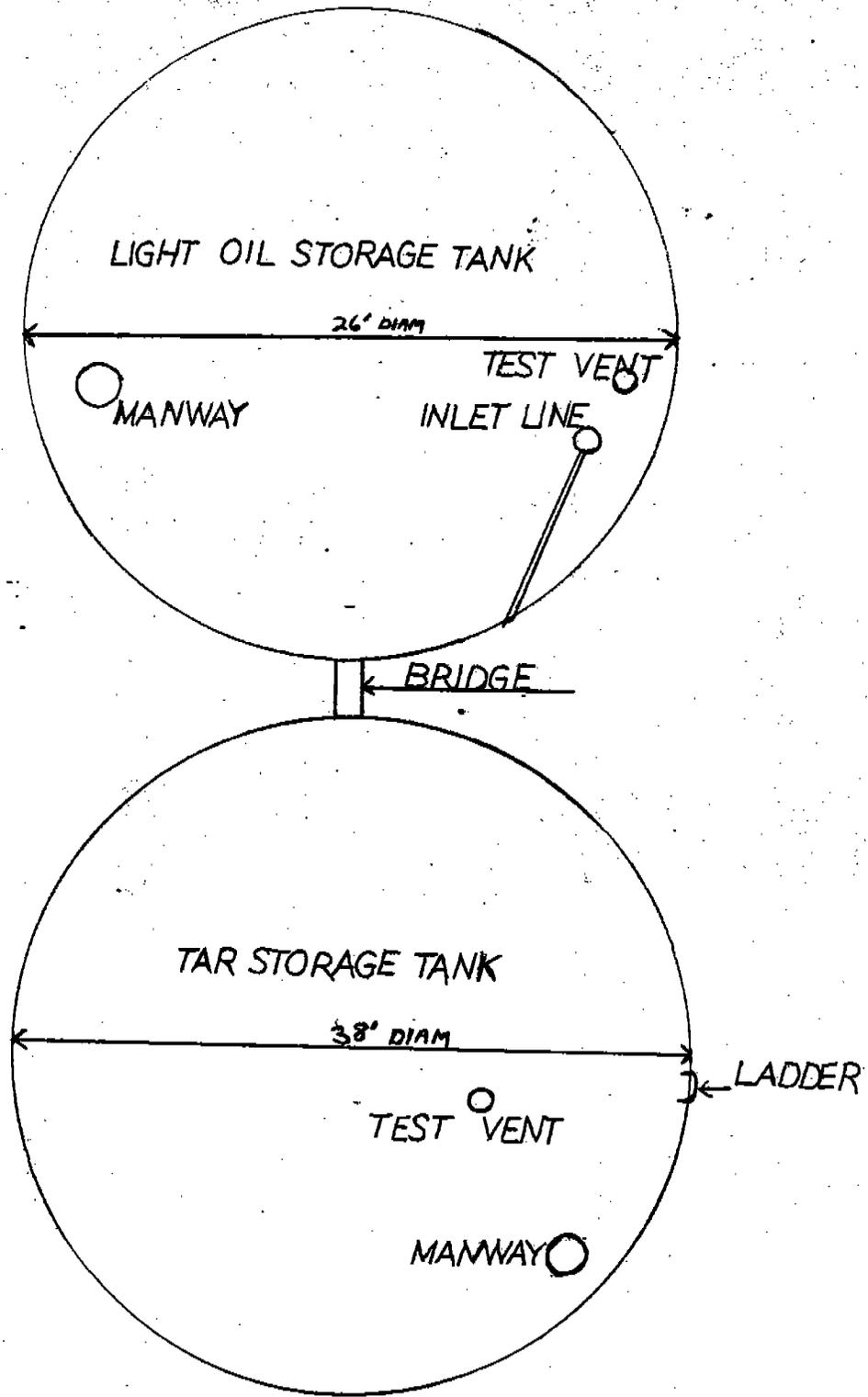
### 6.2 LIGHT OIL STORAGE TANK

The vent on the light oil tank was constructed by the sampling team from two sections of steel stovepipe, fastened to a flange at deck level on the top of the tank. This was necessary in order to obtain accurate velocity readings from tank. The manway, which was found open, was covered during the test runs.

Three half-hour EPA Method 110 tests were run on August 11th and 12th, 1980. Stack temperature was ambient at all times, and no flow rate could be measured with the vane anemometer.

Liquid samples were collected from an inlet to the storage tank via a pump at ground level. The liquid temperature was 25°C (ambient).





NOT TO SCALE

FIGURE 6-1 LIGHT OIL STORAGE TANK AND TAR STORAGE TANK

### 6.3 TAR INTERCEPTING SUMP

Benzene emissions from the tar intercepting sump at Wheeling-Pittsburgh Steel in Monessen, Pennsylvania were measured on 8/12 - 8/13/80 using the tracer method.

The sump was 8' long, 4' wide and 8 1/2' below grade. The liquid was approximately 8" deep and the liquid temperature was 150°F (66°C). There was one major inlet located in the NW corner of the sump approximately 3' above the liquid level. Make-up liquid falling from this height created turbulence over the entire sump but especially in the corner in which it was located. A pump located at the sump's east end was constantly pumping the effluent to the tar decanters, which resulted in a steady flow of material through the sump.

This source was located very close to several large physical obstacles. On the NW corner of the sump was a large building (25' in height) which houses process equipment. On the W and SW sides of the source there was a maze of tanks, pipes and process equipment beginning 5' from the edge of the sump and extending approximately 50' back. This area was sufficiently compact to block any wind from that direction. On the SE corner of the sump 10' from the edge was a pile of pipe approximately 5' in height and 20' long. The NE and N sides of the sump were clear of obstructions. In spite of the degree of congestion in the immediate area there was ample space for sampler placement close to the source on any side.

Wind direction varied widely coming generally from the S. This variability of direction did not seem to alter the direction of emission significantly. Observation of the steam plume rise revealed that the



emissions were confined to the 180° quadrant from W to N over 90% of the time but did vary within that quadrant. The sampling strategy was to bracket the W and N sides of the sump; this was accomplished by placing 4 samplers, 2 on each side, 4' back from the sump edge (See Figure 6-2). The dispersion bar spanned the sump along its 8' length at the liquid level. With this arrangement of samplers and a variable wind, the emissions measured on each side of the sump were different but the average of the total emissions was similar for different sampling runs.



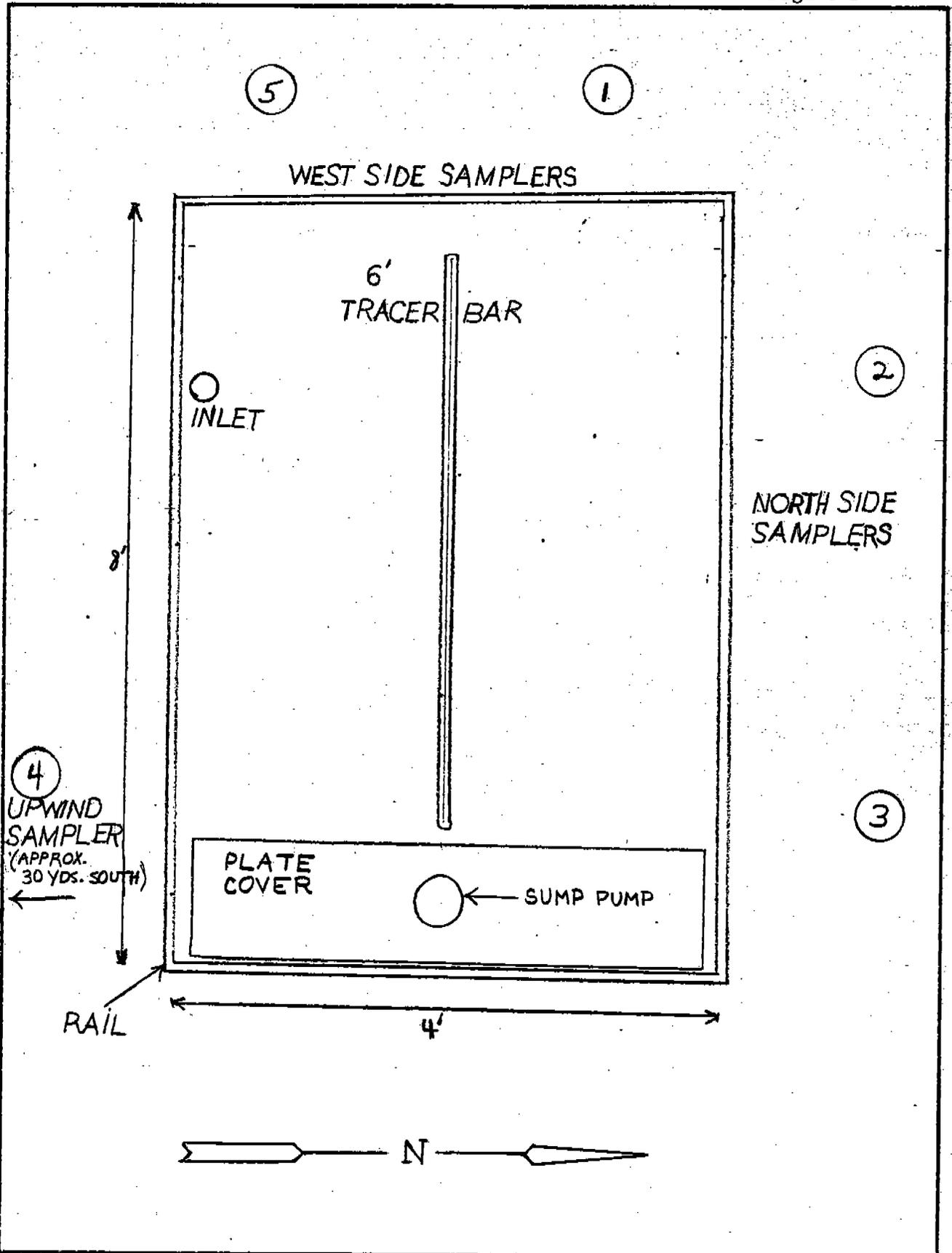


FIGURE 6-2 COMMON TAR INTERCEPTING SUMP

## 7.0 LABORATORY SAMPLE ANALYSIS

Two types of liquid samples were collected: process liquids, and sample line and water trap catches and washes. All liquid samples were stored in amber glass bottles and returned to Scott's Plumsteadville laboratory for analysis.

### 7.1 SAMPLE PREPARATION

Depending upon the complexity of the sample, one of the following sample preparation procedures was followed prior to the "purge and trap" procedure and analysis.

#### Samples Containing Immiscible Liquid Phases

Using a clinical centrifuge (International Equipment Company, Massachusetts) immiscible liquid phases were separated and each phase was analyzed separately for benzene.

#### Samples Containing Solid and Immiscible Liquid Phases

Samples containing solids of higher density than the liquid phase were separated by centrifuge or by simple decantation of the liquid. The different phases in the liquid fraction were then further separated by centrifuging. Solid and liquid phases were analyzed separately.

#### Samples Containing Finely Crystalline Solid Suspension

In analyzing these samples the stoppered sample jars were shaken for at least half an hour for homogenizing the solution. The uniform distribution of suspended fine crystalline solid particles was tested by determining the percentage of dry solid in several aliquots of the homogenized mixture. A weighed amount of the mixture was analyzed for benzene.



### Sampling System Washings

All washings were clear solutions having only one liquid phase. The total weight of the liquid phase was determined using a balance correct to  $\pm 0.1$  g. The total weight of each washing was more than 25 grams, so an error of 0.1 g in weighing the mass will contribute an error of only 0.4% to the final analytical data. A weighed aliquot of the washing was analyzed for benzene by following the "purge and trap" and analysis procedures outlined in the following sections, and using this analysis data the weight of benzene present in the total mass of washing was calculated.

#### 7.2 PURGE AND TRAP PROCEDURE FOR EXTRACTION OF BENZENE FROM LIQUID PHASE TO GASEOUS PHASE

An accurately weighed quantity of the sample to be analyzed was diluted with 20-25 ml of propylene carbonate in a specially designed glass purging apparatus which was kept immersed in a thermostatted water bath maintained at 78°C. Benzene free nitrogen gas was bubbled through the propylene carbonate solution in the purging apparatus at the rate of 0.2 - 0.3 liters/minute, and collected in leak free Tedlar bags. Under these experimental conditions, 1 1/2 - 2 hours were sufficient to purge off all the benzene from the liquid phase to the gaseous phase. The total volume of nitrogen gas used to purge the sample was accurately measured by a calibrated dry gas meter. A diagram of the purge and trap set-up is shown in Figure 7-1.

Propylene carbonate was found to be an ideal diluting solvent for the extraction of benzene from all types of liquid samples containing viscous tar, pitch, light and heavy oil and insoluble particulates. It was chosen for its high boiling point, low density, and good solvating capacity.



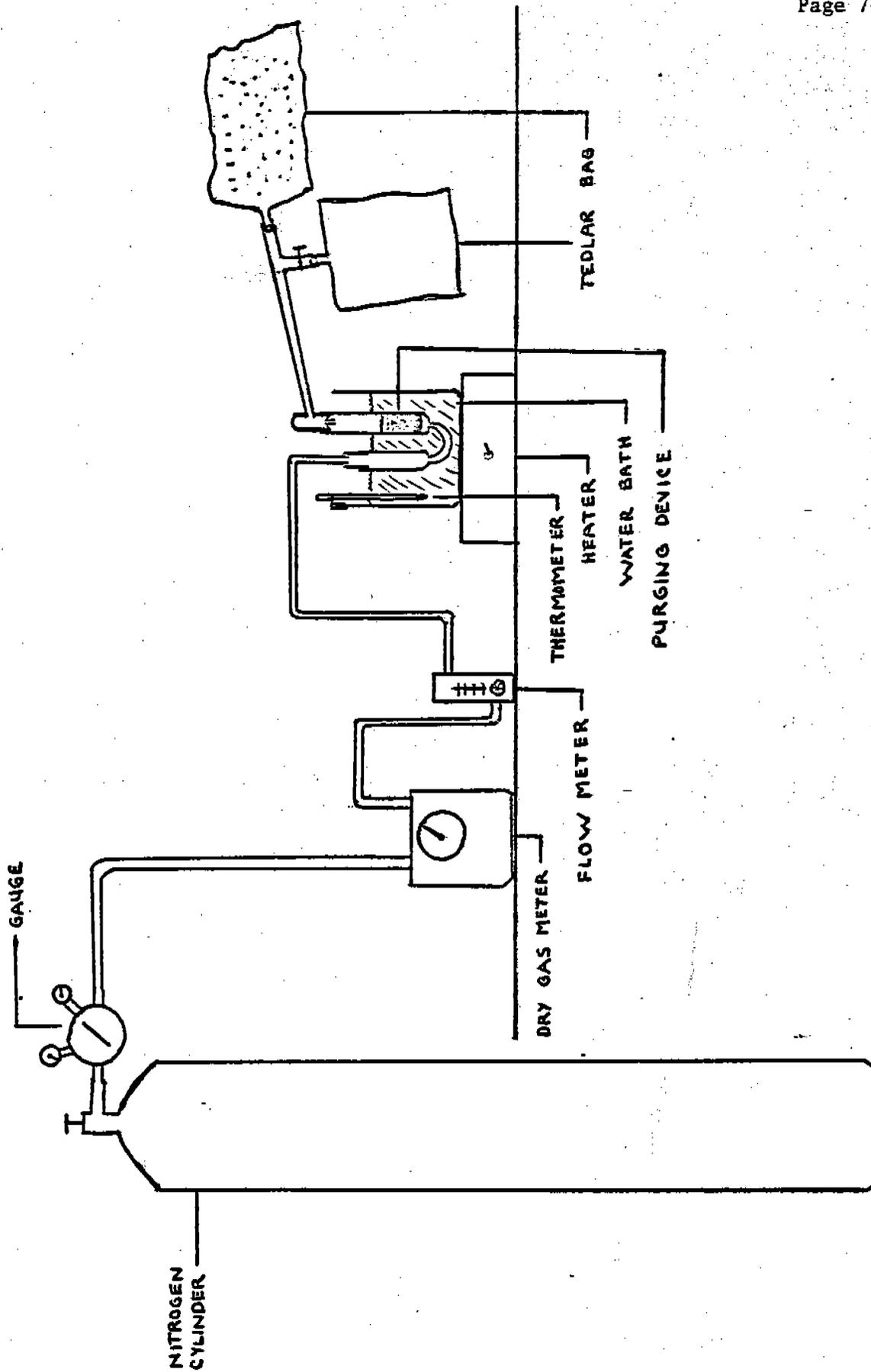


FIGURE 7-1 PURGE AND TRAP METHOD EQUIPMENT SET-UP

### 7.3 GAS CHROMATOGRAPH

A Perkin-Elmer 900 gas chromatograph was used for the analysis of the purge bags. A 10 ft. by 1/8 inch stainless steel column packed with 20% SP-2100/0.1% Carbowax 1500 on 80/120 mesh Supelcoport was used for the analysis. This column gave complete resolution of the benzene peak from other components present in the purge bags. The 'peak height' method was utilized to calculate the concentration of benzene in the purge bags analyzed. The Perkin-Elmer 900 used for analysis was not equipped with a backflushing unit. Gas chromatograph conditions were as follows:

GC column temperature: 70°C isothermal

Detector temperature: 190°C

5 ml loop at a temperature of 120°C

Carrier gas flow rate: 30 cc/min He

Hydrogen flow rate: 45 cc/min

Oxygen flow rate: 400 cc/min

Detector: Flame Ionization Detector (FID)

In addition to benzene, the purge bags contained other volatile hydrocarbons present in the liquid samples such as toluene and naphthalene. Because this chromatograph was not equipped with a backflush, it was necessary to elute all heavy organics from the column by heating the column to 150°C after every two injections for one hour with the carrier gas on. After cooling the column to 70°C the absence of any organic in the column which might overlap the benzene peak in the next analysis was checked. When the column was found to be satisfactorily clean, the next analysis was continued under the conditions previously described.



## 8.0 QUALITY CONTROL AND QUALITY ASSURANCE

The following sections will address quality control and quality assurance procedures for the field analysis of benzene in air samples and the laboratory analysis of process liquids and BaP samples.

### 8.1 FIELD ANALYSIS PROCEDURES

All samples were analyzed in duplicate and as a rule peak heights were reproduced to within 5%. For some very high concentration samples (percent range) it was necessary to make dilutions for analysis. When this was done a fresh dilution was prepared for each injection and peak heights were reproduced to within 10%. To verify that the system was retaining no benzene, frequent injections of the standard and nitrogen were made. In all cases the result was satisfactory.

The Tedlar bags that were reused for sampling were flushed three times with nitrogen and allowed to sit overnight after being filled to approximately three quarters of their capacity. They were analyzed for benzene content the following day. The background concentrations of the bags were recorded and varied from 0 to 10 ppm benzene. Care was taken to use sample bags whose background concentration was very low compared to the expected concentration of the source.

The accuracy and linearity of the gas chromatographic techniques used in this program were tested through the use of EPA Audit Samples. Two standards, a 122.5 ppm and 6.11 ppm benzene were used to analyze the audit cylinders.



## 8.2 PROCEDURES FOR ANALYSIS OF PROCESS LIQUIDS

Scott's benzene standards, checked against EPA Audit Standards, were used as reference standards throughout this program. The accuracy and linearity of the gas chromatographic technique for benzene analysis was tested through the use of EPA Audit Standards which were available to Scott. Gas chromatographic analysis of the samples and standard were performed under identical conditions to assure the accuracy of the analytical data generated.

Each batch of propylene carbonate which was used as the diluting solvent in the purge and trap technique was analyzed for benzene content by subjecting 25 ml of propylene carbonate to the purge and trap procedure followed by gas chromatographic analysis of the trapped gas under identical conditions as described in Section 5.2. All batches of analytical grade propylene carbonate were found to be free from benzene.

Every day before the analysis of samples the purging apparatus and trapping bags were tested for absence of benzene. Whenever the whole system was found to be free from benzene to the lowest detectable limit of the instrument, the samples were analyzed using the purging apparatus and the trapping gas sampling bags.

Generally an accurately weighed mass of each sample was subjected to purge and trap procedure only once and the trapped gas sample was repeatedly analyzed by GC until the analytical data of consecutive GC analyses varied by  $\pm 0.5\%$  or less.



For randomly selected samples, the whole analytical procedure was repeated with a different weighed mass of the source sample to check the validity and accuracy of the analytical methodology. The analytical data for different runs were found not to vary by more than 5%.

By purging the sample with nitrogen under the experimental conditions as utilized by Scott, the recovery of benzene from the sample was quantitative and this has been verified by analyzing a standard benzene solution in propylene carbonate containing tar and pitch.



APPENDIX A  
SAMPLE CALCULATIONS



APPENDIX A  
SAMPLE CALCULATIONS

1. Tracer Gas Calculations

Example: Test 1, Run 1, Sampler-West 1

Concentration of Benzene: 5.78 ppm

Concentration of Isobutane: 2.23 ppm

Isobutane Release Rate: 0.872 lb/hr

Calculation of mass to mass ratios:

$$\text{Benzene } 5.78 \text{ ppm} \times 78 \text{ g/mole} = 450.84$$

$$\text{Isobutane } 2.23 \text{ ppm} \times 58 \text{ g/mole} = 129.34$$

$$\frac{450.84}{129.34} \times 0.872 \text{ lb/hr} = 3.04 \text{ lb/hr benzene}$$

2. Flow Rate at Standard Conditions (Saturated at 68°F, 29.92 inches Hg)

A. Correction for Temperature and Pressure:

$$\text{Flow Rate (STP)} = \text{Flow Rate (Source)} \times \frac{528^{\circ}\text{R}}{\text{T}(\text{°F}) + 460} \times \frac{\text{P}_{\text{bar}} \text{ (in. Hg)}}{29.92}$$

Example: Tar Storage tank, Run 1

$$\text{Flow Rate (STP)} = 19 \text{ cfm} \times \frac{528}{95 + 460} \times \frac{29.18}{29.92} = 17.6 \text{ cfm}$$

B. Correction for Moisture:

Percent moisture (assume saturation at 95°F) = 6%

Percent moisture at standard conditions (Saturated at 68°F) = 2.5%

$$\begin{aligned} \text{Flow Rate (dry)} &= \text{Flow Rate (STP)} \times (100 - \% \text{ Moisture})/100 \\ &= 17.6 \text{ cfm} \times (100 - 6)/100 \\ &= 16.5 \text{ cfm} \end{aligned}$$

$$\begin{aligned} \text{Flow Rate (saturated at 68°F)} &= \text{Flow Rate (dry)} \times 1.025 \\ &= 16.5 \text{ cfm} \times 1.025 \\ &= 17 \text{ cfm} \end{aligned}$$



### 3. Calculation of Mass Emission Rate

Example: Tar storage tank, Run 1

Flow Rate (standard conditions) = 17 cfm

Benzene Concentration: 1043.1 ppm

$$17 \frac{\text{ft}^3}{\text{min}} \times 28.32 \frac{\text{lb}}{\text{ft}^3} \times 60 \frac{\text{min}}{\text{hr}} \times \frac{1043.1}{10^6} \times 78 \frac{\text{lb}}{\text{mole}} \times \frac{1 \text{ mole}}{24.15 \text{ l}} \times \frac{1 \text{ lb}}{454 \text{ g}} = 0.21 \text{ lb/hr}$$



APPENDIX B  
FIELD DATA SHEETS















PROJECT 1906 BENZENE/BaP PRESURVEY

SAMPLE DATA

Plant Wh-Pitt Monessen Process Liq. Samples Date 8/13/80

Sample No. Tar inlet Time Sampled 2:55

Sample Type: Liquid Air

Sample Temperature 71°C

Ambient Temperature \_\_\_\_\_

Description of Sampling Location:

Sample No. L.O. outlet Time Sampled 3:05

Sample Type: Liquid Air

Sample Temperature 25°C (ambient)

Ambient Temperature \_\_\_\_\_

Description of Sampling Location:

Sample No. Tar Storage Time Sampled 3:20

Sample Type: Liquid Air

Sample Temperature 75.5°C

Ambient Temperature \_\_\_\_\_

Description of Sampling Location: dipped from manway on tank.

*mostly flushing liquor*



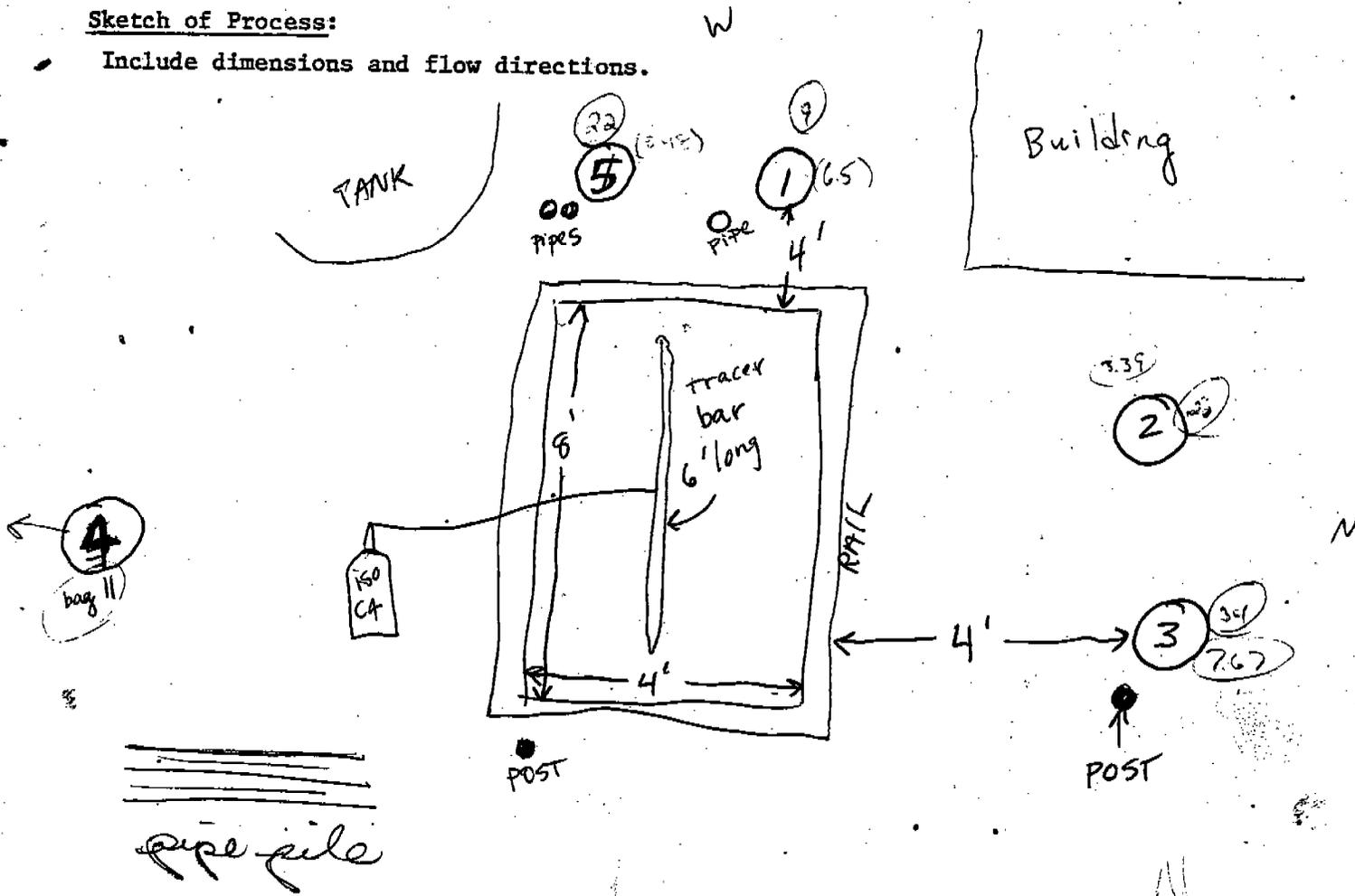
Plant W-Pitt Monessen

Process Common Tar Intercepting Sump

Date 8/12/80

Sketch of Process:

Include dimensions and flow directions.



Process Description:

- 7'8" liquid level to top of sump (ground level)
- 10" liquid depth
- 5' tracer bar level below grade

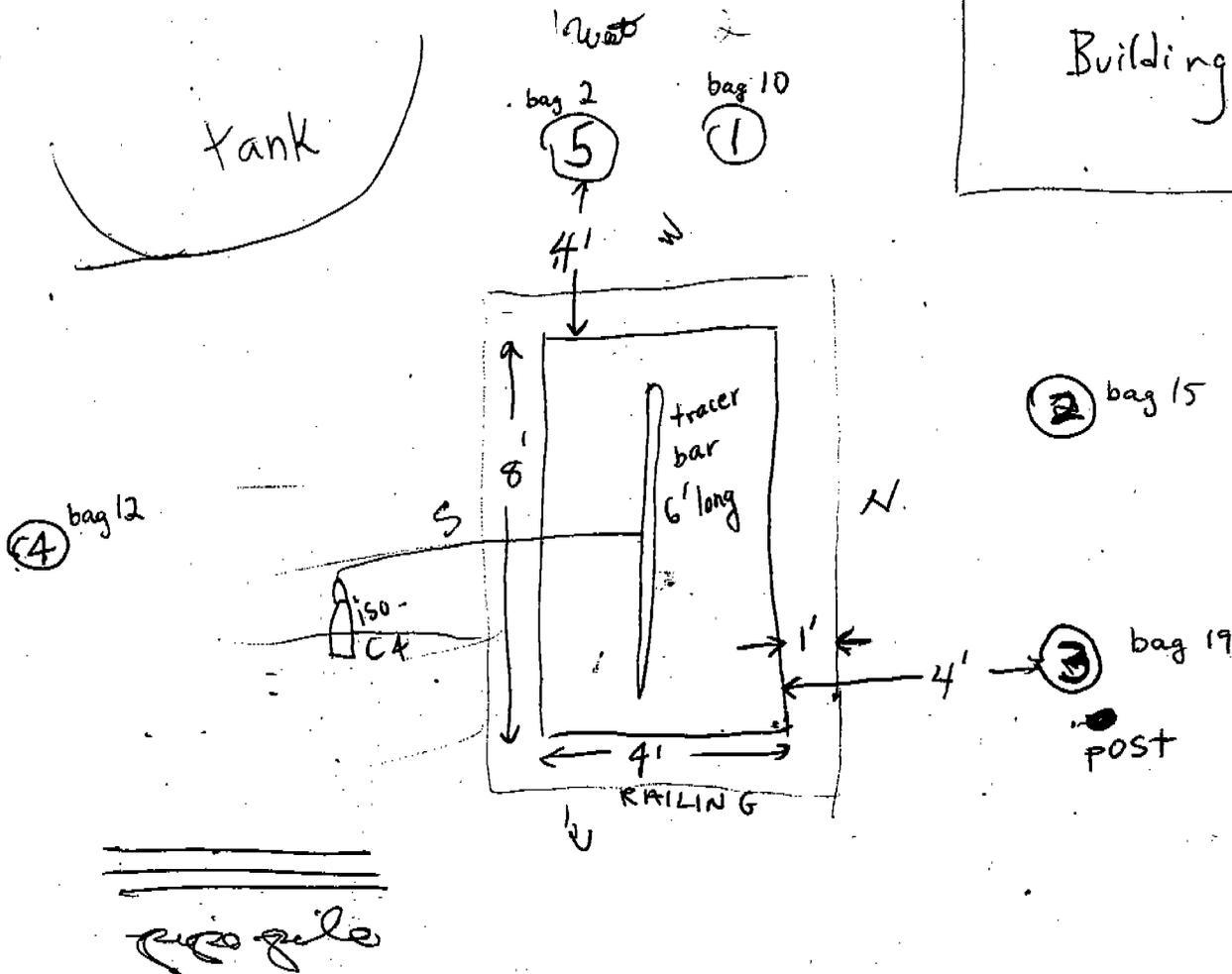




Plant W-P.H MONESSEN Process COMMON THE SUMP Date 8/12/80

Sketch of Process:

Include dimensions and flow directions.



Process Description:

liquid temp ~175 °F  
liquid 8" deep



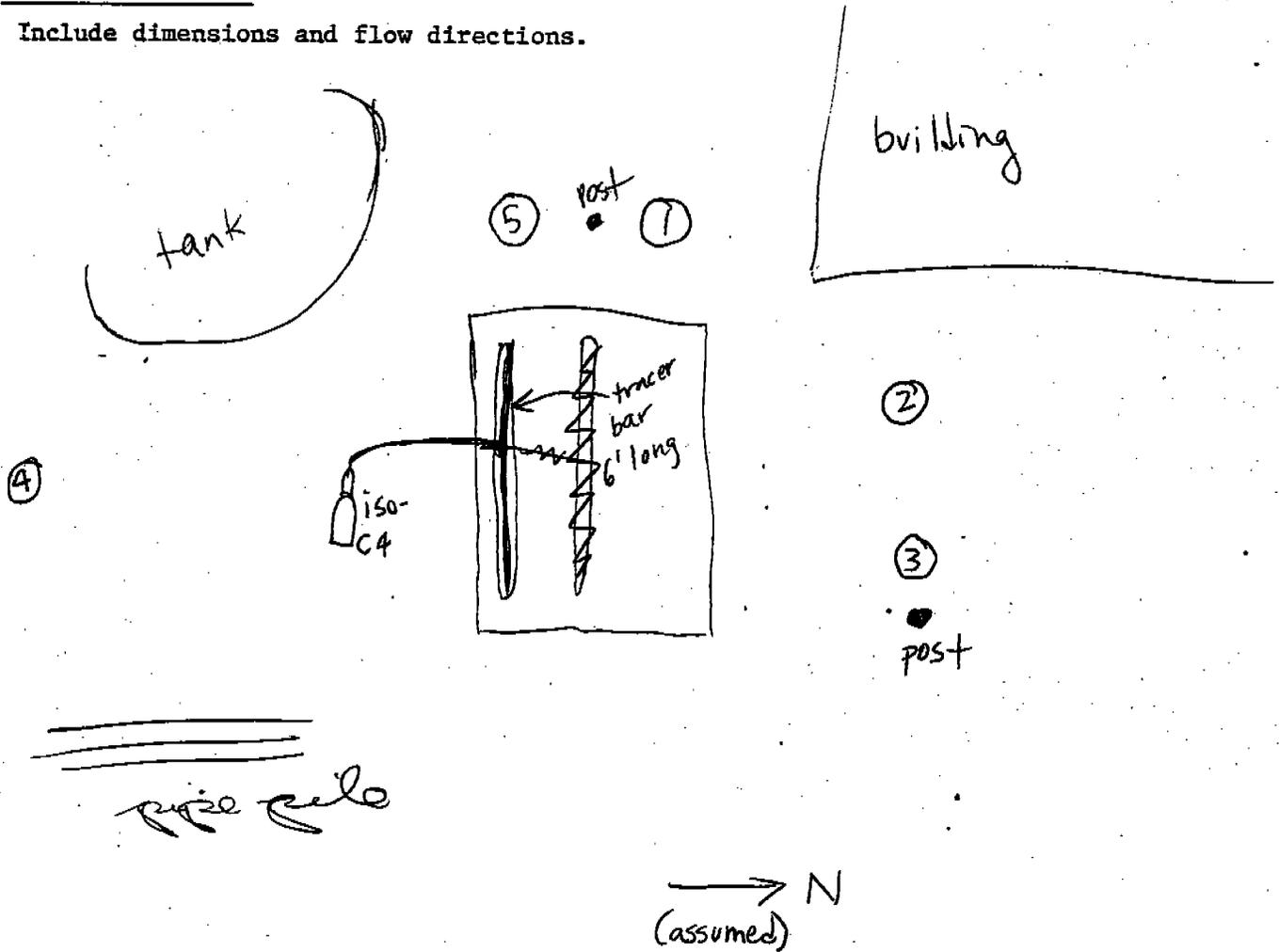


PROJECT 1906 BENZENE/BaP PRESURVEY

Plant Wh-011 Monessen Process Common tar sump Date 8/13/80

Sketch of Process:

Include dimensions and flow directions.



Process Description:

TEST 2  
RUN 2

PROJECT 1922

TRACER GAS DATA SHEET

PLANT: Wh-Ditt Monessen  
 PROCESS: Common Tar Sump  
 PROCESS NOTES:

DATE: 8/13/80  
 WIND SPEED: \_\_\_\_\_  
 WIND DIRECTION: var.  
 AMBIENT TEMPERATURE: \_\_\_\_\_  
 BAROMETRIC PRESSURE: 29.27

Sampler Number  
 Distance from Source  
 Sampling Rate  
 Pump Numbers  
 Tedlar bag numbers  
 Start Time  
 Stop Time

DOWNWIND				UPWIND	
5	1	2	3	4	
4' West	4' west	4' North		50' South	
7	8	16	18	23	

Meter  $\gamma = 1.049$

ISOBUTANE RELEASE: Gas Temperature

TIME	METERED VOLUME
0 11:25	58.300
2	58.535
4	58.787
6	59.040
8	59.284
10	59.521 .122
12	59.755
14	59.977
16	60.205
18	60.434
20	60.657 .110
22	60.900
24	61.148
26	61.389
28	61.622
30	61.852

Gas Pressure

TIME	METERED VOLUME
<u>WIND</u>	
N	
up	
N	
W	
W	
W	
up	
SW	
N	
up	
var.	

$3.552 \text{ ft}^3/30 \text{ min}$

$$\frac{3.786}{30} = .1242 \text{ cfm} = 1.122 \text{ lb/hr.}$$



APPENDIX C  
LABORATORY DATA SHEETS



CHROMATOGRAPHIC ANALYSIS LOG

*M. J. Messer*

Project No. 1922

Date 8-12-80

Analyst JB

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	6.11 <del>mm</del> $\phi$ @ 64x 106 $\mu$ m 1K4 @ 10x	57.5 46.5	.106 1023		
	See Oxygen for Station Inoculated #1 (R un #)				
	Bag # 22 $\phi$ - 64x 1K4 - 32x	545 <del>48.5</del>	.106 .046	578 x 78 = 2.23 x 58 =	450.84 > 3.48 129.34
	Bag # 9 $\phi$ - 16x 1K4 - 8x	47.5 22	.027 .012	1.28 x 78 = 0.26 x 58 =	99.82 > 6.52 15.32
	Bag # 20 $\phi$ - 32x 1K4 - 16x	74.5 68	.053 .033	3.95 x 78 = 1.56 x 58 =	307.98 > 3.39 90.71
	Bag # 34 $\phi$ - 128x 1K4 - 32x	62 48	.212 .046	13.14 x 78 = 2.30 x 58 =	1024.92 > 7.67 133.63
	Bag # 11 $\phi$ - 64x 1K4 - 8x	10.5 25	.053 .012	0.56 x 78 = 0.30 x 58 =	43.41 > 2.50 17.40



CHROMATOGRAPHIC ANALYSIS LOG

*Myonessum Pa*

Project No. 1922

Date 8-12-80

Analyst

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	Std 6.11 ppm @ 64x	56			
	1.06 ppm @ 10x	46.5			
	Tracer test #1, Run #2				
	Bag #2 @ 128x	21.5	.212	4.56 x 78 =	355.68 > 3.33
	104 @ 32x	40	.046	1.84 x 58 =	106.72
	Bag #10 @ 32x	27	.053	1.43 x 78 =	111.54 > 3.80
	104 @ 32x	11	.046	0.50 x 58 =	29.35
	Bag #15 @ 128x	44	.212	9.33 x 78 =	727.58 > 3.03
	104 @ 64x	45	.092	4.14 x 58 =	240.12
	Bag #19 @ 256x	46.5	.424	19.72 x 78 =	1537.85 > 3.07
	104 @ 128x	47	.184	8.65 x 58 =	501.58
	Bag #12 @ 10x	12.5	.027	.338 x 78 =	26.33 > 4.37
	104 @ 10x	4.5	.023	.104 x 58 =	6.03
	Std 6.11 ppm @	56			
	1.06 ppm @ 10x	46			



CHROMATOGRAPHIC ANALYSIS LOG

Monessen Pa.

Project No. 1922

Date 8-12-80

-Analyst

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	Std 122.5 ppm & 128x10 <sup>3</sup>	71.5	1.71 <sup>3.42</sup> 6.85		
	Std Oil Storage Run #1 @ 512x10 <sup>3</sup> Dil 100x	43	6.85	29455 ppm	29455 ppm 2.294%
	Std Oil Storage Run #2 @ 512x10 <sup>3</sup> Dil 100x	33.5	6.85	229.48	22948 ppm 2.29%
	Std 122.5 ppm	72.5			
	Heated Tank Storage Run #1 Dil 10x @ 250x10 <sup>3</sup>	30.5	3.42	10431 ppm	1043 ppm
	Std 122.5 ppm & 128x10 <sup>3</sup> Run #2	48.5	3.42	165.87	1,658.7 ppm
	Std 122.5 ppm & 128x10 <sup>3</sup>	72.5			



CHROMATOGRAPHIC ANALYSIS LOG

M. Messer, Jr.

Project No. 1922

Date 8-13-80

Analyst

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	Std 6.11 µg - 64x 1.00 µg - 16x	57.5 46.5			
	Tracer Test # 2 (Run #1)				
	Box #13 φ 64x 16x 32x	77 63.5	<del>0.105</del> .046	8.09 x 78 = 7.92 x 58 =	630.63 > 3.72 169.42
	Box #14 φ 64x 16x 32x	45 33	.105 .046	4.73 x 78 = 1.52 x 58 =	368.55 > 1/18 88.16
	Box #17 φ 128x 16x 32x	67 81.5	.212 .046	14.20 x 78 = 3.89 x 58 =	1407.91 > 4/91 225.45
	Box #21 φ 64x 16x 32x	32.5 23	.105 .046	3.41 x 78 = 1.06 x 58 =	265.98 > 4.33 61.48
	Box #3 φ 32x 16x 16x	54 43.5	.053 .023	2.86 x 78 = 1.00 x 58 =	223.24 > 3.84 58.0



CHROMATOGRAPHIC ANALYSIS LOG

Monesser Sr

Project No. 1922

Date 8-13-80

Analyst

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	Std 122.5 ppm @ 128x10 <sup>3</sup>	73.5			
	Std oil storage Run #3 512x10 <sup>3</sup> Dil 100x	38	6.68	25384 ppm	25384 ppm <u>2.53%</u>
	Heated Teri Storage 256x10 <sup>3</sup> Dil 10x	83	3.34	27722 ppm	27722 ppm (toluene check high)
	Std 122.5 ppm @ 128x10 <sup>3</sup>	75			



CHROMATOGRAPHIC ANALYSIS LOG

Project No. 1922 Date 8-13-80 Analyst \_\_\_\_\_

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	Stel Collipen $\phi$ 64x 1.06 $\mu$ g/ml 16x Trovan Test $\phi$ 2 Run #2	57 46			
	Bag #7 $\phi$ 128x 164 32x	40 62.5	.212 .046	848 x 78 = 288 x 58 =	661.44 > 3.97 166.75
	Bag #8 $\phi$ 64x 164 32x	44 33.5	.106 .046	466 x 78 = 154 x 58 =	363.48 > 4.07 8938
	Bag #16 $\phi$ 128x 164 32x	48 80.5	.212 .046	1018 x 78 = 370 x 58 =	793.73 > 3.70 21477
	Bag #18 $\phi$ 256x 164 64x	<del>46</del> 62 15.5	.424 .092	1717 x 78 = 478 x 58 =	1339.42 > 4.83 277.47
	Bag #23 $\phi$ 16x 164 16x	4.5	.027 .023	.419 x 78 = .104 x 58 =	32.64 > 5.44 6.00



CHROMATOGRAPHIC ANALYSIS LOG

Monsieur

Project No. 1922

Date 8-13-80

-Analyst

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	Sted 6.11 ppm $\phi$ - 64x 1.06 ppm $\phi$ - 16x Proced. cont #3 Run #1	61 48			
	Bag #9 $\phi$ 128x 164 32x	29 62	.212 .046	6.15 x 78 = 2.85 x 58 =	479.70 > 2.90 165.42
	Bag #10 $\phi$ 64x 164 32x	19.5 22	.106 .046	2.07 x 78 = 1.01 x 58 =	161.23 > 2.75 58.70
	Bag #11 $\phi$ 128x 164 32x	30 67	.212 .046	6.36 x 78 = 3.08 x 58 =	368.88 > 2.06 178.76
	Bag #14 $\phi$ 256x 164 64x	26.5 67	.424 .092	11.24 x 78 = 6.16 x 58 =	876.72 > 2.45 357.51
	Bag #34 $\phi$ 16x 164 16x	12.5 10	.027 -		234 ppm



CHROMATOGRAPHIC ANALYSIS LOG

Project No. 1922

Date 8-13-80

Analyst

Mossman Sa.

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	Std Colligand 64x	63			
	1.06 ppm KCY 16x	49			
	Test #3 Run #2				
	Bag #2 of 64x	50	.106	5.30 x 78 =	413.40 > 3.41
	1KY 32x	45.5	.046	2.09 x 58 =	121.39
	Bag #12 of 64x	21.5	.105	2.26 x 78 =	176.09 > 3.57
	1KY 32x	18.5	.046	0.85 x 58 =	49.36
	Bag #15 of 256x	23	.124	9.75 x 78 =	760.66 > 3.28
	1KY 64x	43.5	.092	4.00 x 58 =	232.12
	Bag #22 of 128x	76	.212	16.11 x 78 =	1256.74 > 3.14
	1KY 64x	75	.092	6.90 x 58 =	400.20
	Bag #20 of 16x 8x	42.5	.027	<del>7.53</del> x 78 =	<del>587.34</del> > 44.85
	1KY 8x	12	.012	0.14 x 58 =	8.12
	Std Colligand 64x	60			
	1.06 ppm KCY	48.5			



APPENDIX D  
TRACER GAS METHOD DEVELOPMENT



Scott Environmental Technology Inc.

## APPENDIX D

## TRACER GAS METHOD DEVELOPMENT

D.1 Tracer Gas Selection

The initial consideration when using the tracer gas method is the choice of a suitable gas. There are several criteria used in the selection: First, the tracer gas must not be present in the atmosphere at the sampling location. Second, the tracer gas must be separable from other components in the background at the sampling location and quantifiable on the same GC column without interfering with the elution of the compound(s) of primary interest. The tracer gas should also be readily available, transportable, economically feasible, and safe for the given usage situation.

For the determination of benzene emissions at secondary by-products plants, isobutane is the recommended tracer gas. The second choice for a tracer gas is a halogenated hydrocarbon. At secondary by-products plants the hydrocarbons in the background atmosphere are almost exclusively emissions from the coking operation and neither isobutane nor halogenated hydrocarbons are present to any significant degree. Isobutane was chosen over a halogenated hydrocarbon on the basis of chromatographic elution characteristics. Isobutane elutes well before the benzene peak thus eliminating any interference when using a temperature program for the chromatographic analysis.

The separation of isobutane from mixtures containing concentrations of hydrocarbons typical of secondary by-products plants was verified by spiking samples collected at different sources in a secondary by-products plant with various concentrations of isobutane and performing

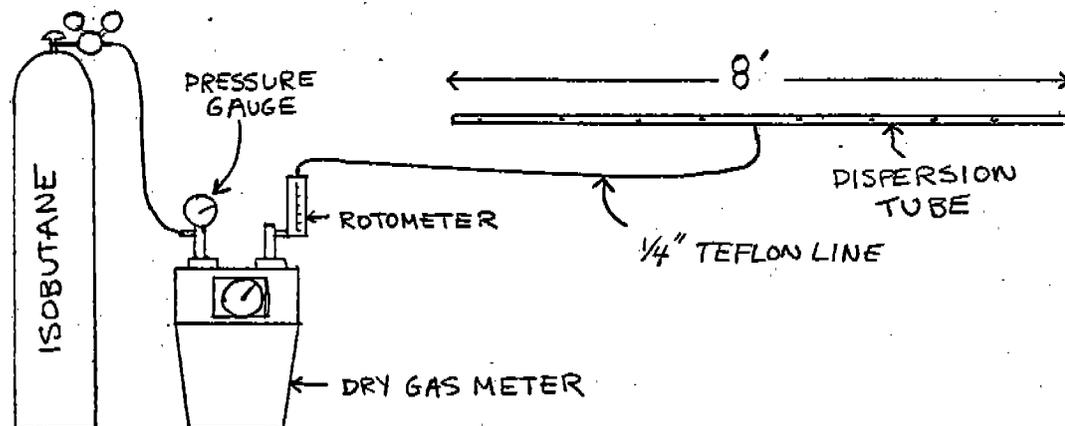


a temperature program of chromatographic analysis to achieve the desired degree of separation. In all cases the desired separation was achieved.

#### D-2 Dispersion Apparatus

The apparatus for the dispersion of tracer consists of a cylinder of the tracer gas connected to a dry gas meter, a rotameter and a dispersion tube. All necessary connecting lines are Teflon.

Two different dispersion tube configurations were tested, both were constructed from 1/4" O.D. stainless steel tubing. The first tube tested was 8' long with the tracer source connected to one end of the tube. The tube contained holes every 19" which were progressively larger moving away from the gas source. The hole size ranged from 0.062" to 0.031". The second tube was 8' long in two 4' sections which are connected via a T-joint to each other and to the tracer gas source. This dispersion tube has 0.041" holes every 19" and the ends are capped.

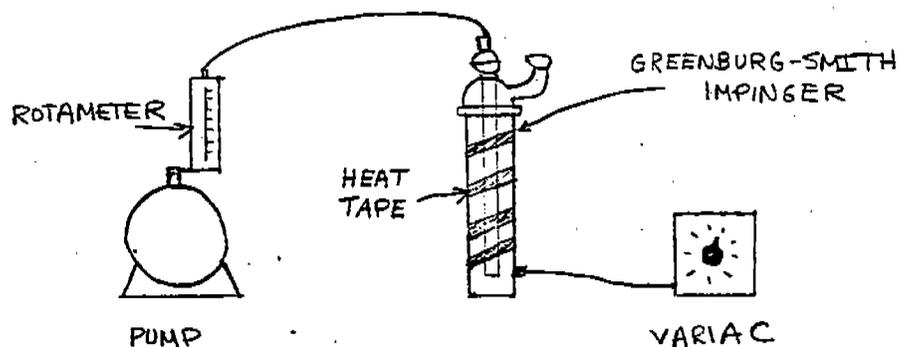


Of the two types of dispersion tubes tested the latter described was more efficient for the dispersion of the tracer. This judgement was made by visual inspection of the holes in each tube while isobutane was flowing at



0.1 CFM. At this rate isobutane can be seen as it leaves the dispersion tube and differences in the relative volume leaving each hole are visually discernible. The first configuration had all gas coming out of the first 2 holes, whereas the second configuration had uniform emissions from each orifice.

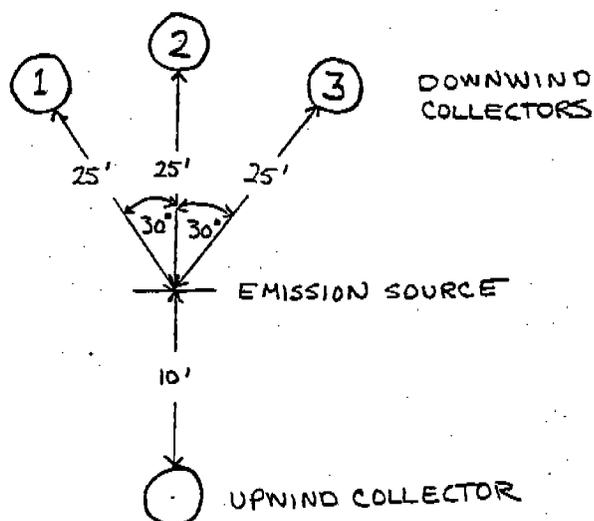
Benzene was also released in two ways; by evaporation and a heated bubbler. Both methods proved adequate for experimental determinations. When evaporation was used to release benzene, a stainless steel pan 16" x 24" x 1/2" was employed to contain the benzene. During an experimental determination benzene was added to the pan in 50 cc aliquots at intervals frequent enough to maintain a constant surface area of benzene. This was done in order to keep the emission of benzene at a constant rate. However, this evaporation method proved unsatisfactory on days when the wind speed exceeded 15-20 MPH due to the changing evaporation rate resulting from gusting wind. A more steady emission of benzene was achieved by using a heated bubbler. The bubbler system consisted of a 500 cc impinger of the Greenburg-Smith design wrapped with a heat tape. The impinger was kept at a constant temperature below the boiling point of benzene. A rubber diaphragm pump was used to push atmospheric air through a bubbler. Flow was regulated with a rotameter.



It was necessary to add more benzene during an experimental run, because the emission rate drops substantially if the benzene level drops too low in the impinger. The frequency of addition and the quantity of benzene per addition are dependent on the emission rate being used. For our determinations it was necessary to add 50 cc of benzene at intervals of approximately 10 minutes.

### D-3 Experimental Determinations

An experiment consists of the release of a known amount of isobutane and benzene simultaneously. Samples are collected along a  $30^\circ$  arc, 25 feet downwind from the source of the emissions.



Initially samples were grab samples collected in clean one liter glass gas flasks. Later samples were integrated over a 1/2 hour period and collected in clean 10-liter Tedlar bags via Emission Measurements Air Quality Sampler with a flow rate of 10 LPH.

In initial determinations, portions of actual presurvey samples containing 62% benzene were released in an effort to simulate



the type of sample which would be encountered in the field. Various amounts of the sample mixture from 0.20 to 10 cc were released and samples were collected downwind in 1-liter gas flasks. When these samples were analyzed the amount of benzene detected was very small, approximately 20 ppb. From this it was apparent that it would be necessary to release significantly more benzene in order to produce the necessary concentration at the sampling location so that quantitative mass to mass ratios could be calculated.

Because of the necessity of releasing more benzene and avoiding the foul odor which the high concentration benzene field samples possessed, it was decided that pure benzene be used for all subsequent determinations.

For the next series of experiments evaporation as previously described was used to release benzene. This series of experiments produced results accurate to within 10% of the theoretical mass to mass ratios with a minimum benzene emission of 0.54 lb/hr for the series. These experiments were performed on days when the wind speed was light (5 - 10 MPH) and the wind direction was steady (See Table D-1).

The next experiment was designed to test the variations which might be introduced when the wind speed and direction were less than favorable. On the day selected the wind speed was 20-25 MPH and the direction was 180° variable due to a changing weather system. The rate of evaporation of the benzene was noticeably affected by the conditions as were the dispersion patterns of the emissions. Erratic results were produced by the meteorological stress on key experimental variables. Calculated mass to mass ratios differed from the theoretical value from 15% to as much as 56%, demonstrating the effect of high and variable winds on the technique. In order to reduce stress on the experiment the benzene bubbler as described was used to provide



a steady source of benzene emission at a rate that would be independent of meteorological conditions. On the day chosen to use the bubbler system the wind speed was 15-20 MPH and the direction was steady. Favorable results were obtained despite the relatively strong wind demonstrating that the tracer technique is valid in winds up to 20 MPH depending on the sampling location (see Table D-1).

#### D-4 Summary

When using the tracer gas method it is necessary to verify that the tracer gas is detectable at the sampling location of choice as the method is somewhat dependent upon meteorological conditions. The method works best when the wind speed is light to moderate, 5-15 MPH, and the wind direction is steady. When the wind speed exceeds approximately 20 MPH or if there is no wind and/or the wind direction is too variable, dispersion patterns conducive to accurate sampling are disturbed and quantitative mass to mass relationships are difficult to establish. The upper limit of stress with respect to meteorological conditions can be examined by the spread of mass to mass ratios for each individual sample for a given sampling run. If the calculated ratios are inconsistent or the deviation between each calculated ratio and their mean is greater than 20%, it would be necessary to seek an explanation based on process variations or meteorological conditions or to void the sampling run and possibly suspend sampling until conditions are more favorable.

#### D-5 Field Sampling Strategy

The program for a sampling run will generally involve the collection of triplicate downwind samples and a single point upwind sample. Actual sampler locations will be determined by the gas chromatograph on



site. Grab samples will be collected in glass flasks and analyzed to determine the benzene concentration in the vicinity of the source to be tested. This information will be correlated with wind speed and direction to choose the exact sampler locations. In the ideal case downwind samplers will be equidistant from the source and along approximately a  $30^{\circ}$  arc.

Two sets of samples will be integrated over separate one-half hour periods and together constitute a single test. Samples will be collected by Environmental Measurements AQS II sampling system into clean 10-liter Tedlar bags. Tedlar bags to be reused for sampling will be flushed three times with nitrogen and allowed to sit overnight three quarters full. Prior to their next use each will be analyzed for benzene content.

The tracer gas dispersion apparatus will be positioned over the source to be tested as near as possible to the actual emissions. Ideally the dispersion tube or support member will span the source of the emissions at its center.



TABLE D-1  
EXPERIMENTAL DATA

Release Rate g/min	Benzene Release Method	Sample Type	Wind Speed	Wind Direction	Theoretical $T\phi/ic_4$	$\phi/ic_4$ #1	$\phi/ic_4$ #2	$\phi/ic_4$ #3	Average
$\phi$ 0.027 $ic_4$ 5.26	Evaporation	Grab	0-5 MPH	Steady	0.005	*NO	NO	NO	----
$\phi$ 0.993 $ic_4$ 8.27	Evaporation	Grab	0-5 MPH	Steady	0.120	*NO	NO	NO	----
$\phi$ 4.05 $ic_4$ 7.16	Evaporation	Grab	0-5 MPH	Steady	0.59	0.64	0.64	0.65	0.645
$\phi$ 9.40 $ic_4$ 6.38	Evaporation	Integrated	5-10 MPH	Steady	1.47	1.57	1.43	----	1.50
$\phi$ 10.85 $ic_4$ 13.59	Evaporation	Integrated	20-25 MPH	Variable	0.80	1.29	1.82	0.94	1.35
$\phi$ 9.40 $ic_4$ 8.25	Bubbler	Integrated	15-20 MPH	Steady	1.14	1.40	1.93	1.02	1.18
$\phi$ 6.33 $ic_4$ 6.48	Bubbler	Integrated	0-5 MPH	Steady	0.91	0.97	0.96	0.96	0.96
$\phi$ 6.48 $ic_4$ 6.48	Bubbler	Integrated	0-5 MPH	Steady	1.00	0.91	0.86	0.89	0.89

$\phi$  - Benzene

$ic_4$  - Isobutane

\* No benzene, only isobutane detected.



APPENDIX E  
PROJECT PARTICIPANTS



APPENDIX E

PROJECT PARTICIPANTS

The following people participated in some phase of the sampling program at Wheeling-Pittsburgh Steel:

From Scott Environmental Technology, Inc.:

Tom Bernstiel, Chemist

Jack Carney, Chemist

P. K. Chattopadhyay, Chemist

Dan FitzGerald, Manager, Eastern Operations

Kevin Gordon, Technician

Carolyn Graham, Chemical Engineer

Lou Reckner, Vice President and General Manager

From Research Triangle Institute:

David Pasquini



APPENDIX F  
EPA Method 110



(f) All continuous monitoring systems used in accordance with this section are to complete a minimum of one cycle of operation (sampling, analyzing, and data recording) for each successive 15-minute period.

(g) Owners or operators of all continuous monitoring systems installed in accordance with this subpart shall check the zero and span drift at least once daily in accordance with the method prescribed by the manufacturer of such systems unless the manufacturer of such systems recommends adjustments at shorter intervals, in which case such recommendations shall be followed. The daily span check is to be conducted with reference gas containing a concentration of benzene determined to be equivalent to the emission limit for that source based on the emission tests required by § 61.94.

(h) The calibration is to be done with either—

(1) A calibration mixture prepared from the liquids and gases specified in Section 5.2.1 and 5.2.2 of Test Method 110 and in accordance with Section 7.1 of Test Method 110; or

(2) A calibration gas cylinder standard containing the appropriate concentration of benzene. The gas composition of the calibration gas cylinder standard is to have been certified by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so gas standards will not be used if their concentration has changed greater than  $\pm 5$  percent from the certified value. The date of gas cylinder preparation, certified benzene concentration, and recommended maximum shelf life must have been affixed to the cylinder before shipment from the manufacturer to the buyer. If a gas chromatograph is used as the continuous monitoring system, these gas mixtures may be used directly to prepare a chromatograph calibration curve as described in Section 7.2 of Test Method 110 for certification of cylinder standards and for establishment and verification of calibration standards.

(i) After receipt and consideration of written application, the Administrator may approve use of an alternative or equivalent continuous monitoring system, alternative monitoring procedures, or alternative monitoring requirements.

(Sec. 114, Clean Air Act as amended [42 U.S.C. 7414])

#### § 61.96 Recordkeeping requirements.

(a) The owner or operator of each source to which this subpart applies shall maintain daily records of the monitoring information specified in § 61.95(a).

(b) Records are to be retained at the source and made available for inspection by the Administrator for a minimum of 2 years.

(Sec. 114, Clean Air Act as amended [42 U.S.C. 7414])

#### Appendix B—Test Methods

##### Method 110. Determination of Benzene From Stationary Sources

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to benzene, a carcinogen.

#### 1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of benzene in stack gases from processes as specified in the regulations. The method does not remove benzene contained in particulate matter.

1.2 Principle. An integrated bag sample of stack gas containing benzene and other organics is subjected to gas chromatographic (GC) analysis, using a flame ionization detector (FID).

#### 2. Range and Sensitivity

The range of this method is 0.1 to 70 ppm. The upper limit may be extended by extending the calibration range or by diluting the sample.

#### 3. Interferences

The chromatograph columns and the corresponding operating parameters herein described normally provide an adequate resolution of benzene; however, resolution interferences may be encountered on some sources. Therefore, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis problem, subject to the approval of the Administrator. Approval is automatic provided that the tester produces confirming data through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and has the data available for review by the Administrator.

#### 4. Apparatus

4.1 Sampling (see Figure 110-1). The sampling train consists of the following components:

4.1.1 Probe. Stainless steel, Pyrex\* glass, or Teflon tubing (as stack temperature permits), equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample Lines. Teflon, 6.4 mm outside diameter, of sufficient length to connect probe to bag. Use a new unused piece for each series of bag samples that constitutes an emission test and discard upon completion of the test.

4.1.3 Quick Connects. Stainless steel, male (2) and female (2), with ball checks (one

pair without) located as shown in figure 110-1.

4.1.4 Tedlar or aluminized Mylar bags, 100 L capacity, to contain sample.

4.1.5 Bag Containers. Rigid leakproof containers for sample bags with covering to protect contents from sunlight.

4.1.6 Needle Valve. To adjust sample flow rate.

4.1.7 Pump. Leak-free with minimum of 2 L/min capacity.

4.1.8 Charcoal Tube. To prevent admission of benzene and other organics to the atmosphere in the vicinity of samplers.

4.1.9 Flow Meter. For observing sample flow rate; capable of measuring a flow range from 0.10 to L/min.

4.1.10 Connecting Tubing. Teflon, 6.4 mm outside diameter, to assemble sampling train (Figure 110-1.)

4.2 Sample Recovery. Teflon tubing, 6.4 mm outside diameter, is required to connect chromatograph sample loop for sample recovery. Use a new unused piece for each series of bag samples that constitutes an emission test and discard upon conclusion of analysis of those bags.

4.3 Analysis. The following equipment is needed:

4.3.1 Gas Chromatograph. With FID, potentiometric strip chart recorder and 1.0 to 2.0 mL sampling loop in automatic sample valve. The chromatographic system shall be capable of producing a response to 0.1ppm benzene that is at least as great as the average noise level. (Response is measured from the average value of the base line to the maximum of the waveform, while standard operating conditions are in use.)

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\* Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.

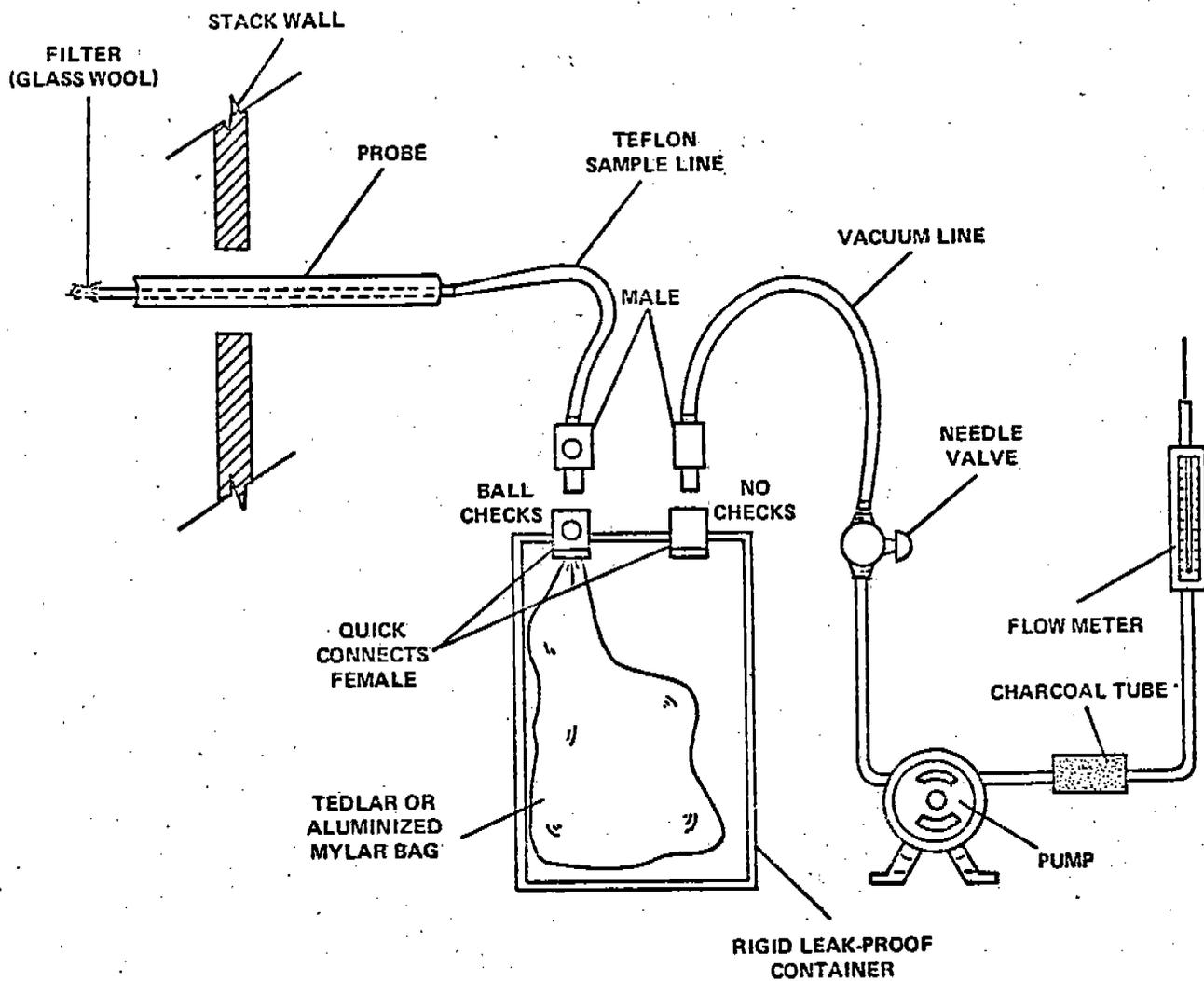


Figure 110-1. Integrated-bag sampling train. (Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.)

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**4.3.2 Chromatographic Columns.** Columns as listed below. The analyst may use other columns provided that the precision and accuracy of the analysis of benzene standards are not impaired and he has available for review information confirming that there is adequate resolution of the benzene peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the benzene peak by an interferent peak. Calculation of area overlap is explained in Appendix E, Supplement A: "Determination of Adequate Chromatographic Peak Resolution.")

**4.3.2.1 Column A: Benzene in the Presence of Aliphatics.** Stainless steel, 2.44 m by 3.2 mm, containing 10 percent 1,2,3-tris (2-cyanoethoxy) propane (TCEP) on 80/100 Chromosorb P AW.

**4.3.2.2 Column B: Benzene With Separation of the Isomers of Xylene.** Stainless steel, 1.83 m by 3.2 mm, containing 5 percent SP 1,200/1.75-percent Bentone 34 on 100/120 Suplecoport.

**4.3.3 Flow Meters (2).** Rotameter type, 100 mL/min capacity.

**4.3.4 Gas Regulators.** For required gas cylinders.

**4.3.5 Thermometer.** Accurate to 1° C, to measure temperature of heated sample loop at time of sample injection.

**4.3.6 Barometer.** Accurate to 5 mmHg, to measure atmospheric pressure around gas chromatograph during sample analysis.

**4.3.7 Pump.** Leak-free, with minimum of 100 mL/min capacity.

**4.3.8 Recorder.** Strip chart type, optionally equipped with either disc or electronic integrator.

**4.3.9 Planimeter.** Optional, in place of disc or electronic integrator, on recorder, to measure chromatograph peak areas.

**4.4 Calibration.** Sections 4.4.2 through 4.4.5 are for the optional procedure in Section 7.1.

**4.4.1 Tubing.** Teflon, 6.4 mm outside diameter, separate pieces marked for each calibration concentration.

**4.4.2 Tedlar or Aluminized Mylar Bags.** 50 L capacity, with valve; separate bag marked for each calibration concentration.

**4.4.3 Syringes.** 1.0  $\mu$ L and 10  $\mu$ L, gas tight, individually calibrated to dispense liquid benzene.

**4.4.4 Dry Gas Meter, With Temperature and Pressure Gauges.** Accurate to  $\pm 2$  percent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flow rate used to prepare standards.

**4.4.5 Midget Impinger/Hot Plate Assembly.** To vaporize benzene.

## 5. Reagents

Use only reagents that are of chromatographic grade.

**5.1 Analysis.** The following are needed for analysis:

**5.1.1 Helium or Nitrogen.** Zero grade, for chromatograph carrier gas.

**5.1.2 Hydrogen.** Zero grade.

**5.1.3 Oxygen or Air.** Zero grade, as required by the detector.

**5.2 Calibration.** Use one of the following options: either 1.2.1 and 5.2.2, or 5.2.3.

**5.2.1 Benzene, 99 Mol Percent Pure.** Certified by the manufacturer to contain a

minimum of 99 Mol percent benzene; for use in the preparation of standard gas mixtures as described in Section 7.1.

**5.2.2 Nitrogen.** Zero grade, for preparation of standard gas mixtures as described in Section 7.1.

**5.2.3 Cylinder Standards (3).** Gas mixture standards (50, 10, and 5 ppm benzene in nitrogen cylinders). The tester may use cylinder standards to directly prepare a chromatograph calibration curve as described in Section 7.2.2, if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of  $\pm 3$  percent or better (see Section 5.2.3.1). (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than  $\pm 5$  percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified benzene concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

**5.2.3.1 Cylinder Standards Certification.** The manufacturer shall certify the concentration of benzene in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration calibration standard (between 50 and 100 ppm) to prepare his calibration curve by an appropriate dilution technique; and (2) a low-concentration calibration standard (between 5 and 10 ppm) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source of error and correct it, then repeat the three-point calibration.

**5.2.3.2 Verification of Manufacturer's Calibration Standards.** Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared (with 99 Mol percent benzene) in accordance with the procedure described in Section 7.1 or by (b) having it analyzed by the National Bureau of Standards. The agreement between the initially determined concentration value and the verification concentration value must be within  $\pm 5$  percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

**5.2.4 Audit Cylinder Standards (2).** Gas mixture standards with concentrations known only to the person supervising the analysis of samples. The audit cylinder standards shall be identically prepared as those in Section 5.2.3 (benzene in nitrogen cylinders). The concentrations of the audit cylinder should be: one low-concentration cylinder in the range of 5 to 20 ppm benzene and one high-concentration cylinder in the range of 100 to 300 ppm benzene. When available, the tester may obtain audit cylinders by contacting: U.S. Environmental

Protection Agency, Environmental Monitoring and Support Laboratory, Quality Assurance Branch (MD-77), research Triangle Park, North Carolina 27711. If audit cylinders are not available at the Environmental Protection Agency, the tester must secure an alternative source.

## 6. Procedure

**6.1 Sampling.** Assemble the sample train as shown in Figure 110-1. Perform a bag leak check according to Section 7.3.2. Join the quick connects as illustrated, and determine that all connections between the bag and the probe are tight. Place the end of the probe at the centroid of the stack, and start the pump with the needle valve adjusted to yield a flow that will more than half fill the bag in the specified sample period. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. At all times, direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

**6.2 Sample Storage.** Keep the sample bags out of direct sunlight. Perform the analysis within 4 days of sample collection.

**6.3 Sample Recovery.** With a new piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to receive gas from the bag through the sample loop. Arrange the equipment so the sample gas passes from the sample valve to a 100-mL/min rotameter with flow control valve followed by a charcoal tube and a 1-in. pressure gauge. The tester may maintain the sample flow either by a vacuum pump or container pressurization if the collection bag remains in the rigid container. After sample loop purging is ceased, always allow the pressure gauge to return to zero before activating the gas sampling valve.

**6.4 Analysis.** Set the column temperature to 80° C (176° F) for column A or 75° C (167° F) for column B, and the detector temperature to 225° C (437° F). When optimum hydrogen and oxygen flow rates have been determined, verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 20 mL/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base-line drift has ceased. Purge the sample loop for 30 sec at the rate of 100 mL/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed, and the attenuator setting. From the chart, note the peak having the retention time corresponding to benzene, as determined in Section 7.2.1. Measure the benzene peak area,  $A_m$ , by use of a disc integrator, electronic integrator, or a planimeter. Record  $A_m$  and

the retention time. Repeat the injection at least two times or until two consecutive values for the total area of the benzene peak do not vary more than 5 percent. Use the average value of these two total areas to compute the bag concentration.

**6.5 Determination of Bag Water Vapor Content.** Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.)

#### **7. Preparation of Standard Gas Mixtures, Calibration, and Quality Assurance**

**7.1 Preparation of Benzene Standard Gas Mixtures.** (Optional procedure—delete if cylinder standards are used.) Assemble the apparatus shown in Figure 110-2. Evacuate a 50-L Tedlar or aluminized Mylar bag that has passed a leak check (described in Section 7.3.2) and meter in about 50 L of nitrogen. Measure the barometric pressure, the relative pressure at the dry gas meter, and the temperature at the dry gas meter. While the bag is filling, use the 10 $\mu$ L syringe to inject 10 $\mu$ L of 99+ percent benzene through the septum on top of the impinger. This gives a concentration of approximately 50 ppm of benzene. In a like manner, use the other syringe to prepare dilutions having approximately 10 ppm and 5 ppm benzene concentrations. To calculate the specific concentrations, refer to Section 8.1. These gas mixture standards may be used for 7 days from the date of preparation, after which time preparation of new gas mixtures is required. (Caution: If the new gas mixture standard is a lower concentration than the previous gas mixture standard, contamination may be a problem when a bag is reused.)

#### **7.2 Calibration.**

**7.2.1 Determination of Benzene Retention Time.** (This section can be performed simultaneously with Section 7.2.2.) Establish chromatograph conditions identical with those in Section 6.4, above. Determine proper attenuator position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed, and the attenuator setting. Record peaks and detector responses that occur in the absence of benzene. Maintain conditions, with the equipment plumbing arranged identically to Section 6.3, and flush the sample loop for 30 sec at the rate of 100 mL/min with one of the benzene calibration mixtures. Then activate the sample valve. Record the injection time. Select the peak that corresponds to benzene. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This distance divided by the chart speed is defined as the benzene peak retention time. Since it is quite likely that there will be other organics present in the sample, it is very important that positive identification of the benzene peak be made.

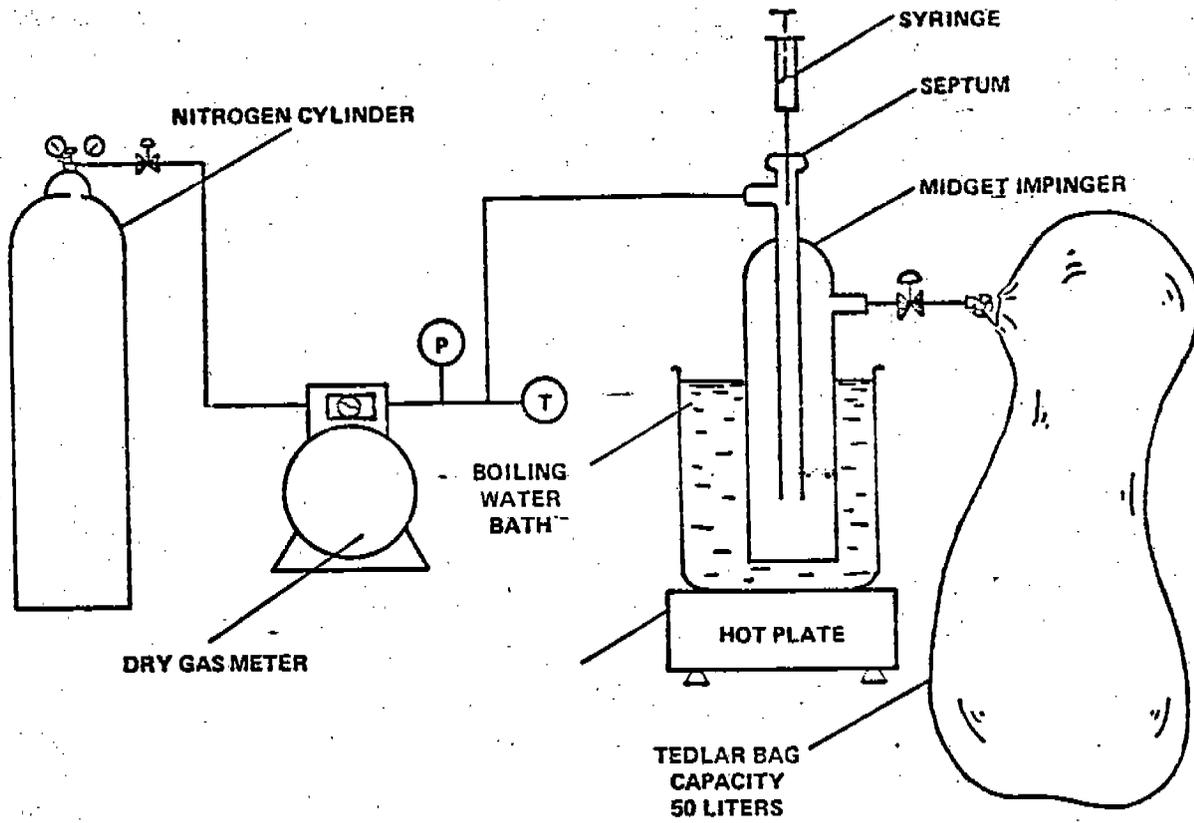


Figure 110-2. Preparation of benzene standards (optional).

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**Question.**

7.2.2 Preparation of Chromatograph Calibration Curve. Make a gas chromatographic measurement of each standard gas mixture (described in Section 5.2.3 or 7.1.1) using conditions identical with those listed in Sections 6.3 and 6.4. Flush the sampling loop for 30 sec at the rate of mL/min with one of the standard gas mixtures and activate the sample valve. Record  $C_c$ , the concentration of benzene injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate  $A_c$ , the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two values versus  $C_c$ . When the other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points derived by the least squares method. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

**7.3 Quality Assurance.**

7.3.1 Analysis Audit. Immediately after the preparation of the calibration curve and before the sample analyses, perform the

analysis audit described in Appendix E, Supplement B: "Procedure for Field Auditing GC Analysis."

7.3.2 Bag Leak Checks. While performance of this section is required after bag use, it is also advised that it be performed before bag use. After each use, make sure a bag did not develop leaks by connecting a water manometer and pressurizing the bag to 5 to 10 cm H<sub>2</sub>O (2 to 4 in. H<sub>2</sub>O). Allow to stand for 10 min. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: an alternative leak check method is to pressurize the bag to 5 to 10 cm H<sub>2</sub>O or 2 to 4 in. H<sub>2</sub>O and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

**8. Calculations**

8.1 Optional Benzene Standards Concentrations. Calculate each benzene standard concentration ( $C_c$  in ppm) prepared in accordance with Section 7.1 as follows:

$$C_c = \frac{B(0.2706)(10^3)}{V_m Y \frac{293}{T_m} \frac{P_m}{760}}$$

$$C_c = 701.9 \frac{BT_m}{V_m Y P_m} \quad (110-1)$$

where:

- B = Volume of benzene injected, microliters.  
 $V_m$  = Gas volume measured by dry gas meter, liters.  
 Y = Dry gas meter calibration factor, dimensionless.  
 $P_m$  = Absolute pressure of the dry gas meter, mmHg.  
 $T_m$  = Absolute temperature of the dry gas meter, °K.  
 0.2706 = Ideal gas volume of benzene at 293° K and 760 mmHg L/mL.  
 $10^3$  = Conversion factor [(ppm)(mL)/μL].

8.2 Benzene Sample Concentrations. From the calibration curve described in Section 7.2.2 above, select the value of  $C_c$  that corresponds to  $A_c$ . Calculate the concentration of benzene in the sample ( $C_s$  in ppm) as follows:

$$C_s = \frac{C_c P_r T_i}{P_i T_r (1 - S_{wb})} \quad (110-2)$$

where:

- $C_s$  = Concentration of benzene in the sample, ppm.  
 $C_c$  = Concentration of benzene indicated by the gas chromatograph, ppm.  
 $P_r$  = Reference pressure, the barometric pressure recorded during calibration, mmHg.  
 $T_i$  = Sample loop temperature at the time of analysis, °K.  
 $P_i$  = Barometric pressure at time of analysis, mmHg.  
 $T_r$  = Reference temperature, the sample loop temperature recorded during calibration, °K.  
 $S_{wb}$  = Water vapor content of the bag sample, volume fraction.

**9. References**

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4. Current Peaks. 10:1. Carle Instruments, Inc. Fullerton, Calif. 1977.
5. Knoll, Joseph E. Communications Concerning Chromatographic Columns for Benzene Analysis. October 18, 1977.
6. Knoll, Joseph E. Communications Concerning Gas Chromatographic Columns for Separating Benzene From Other Organics in Cumene and Maleic Anhydride Process Effluents. November 10, 1977.

**Appendix C****Supplement A—Determination of Adequate Chromatographic Peak Resolution**

In this method of dealing with resolution, the extent to which one chromatographic peak overlaps another is determined.

For convenience, consider the range of the elution curve of each compound as running from  $-2\sigma$  to  $+2\sigma$ . This range is used in other resolution criteria, and it contains 95.45 percent of the area of a normal curve. If two peaks are separated by a known distance,  $b$ , one can determine the fraction of the area of one curve that lies within the range of the other. The extent to which the elution curve of a contaminant compound overlaps the curve of a compound that is under analysis is found by integrating the contaminant curve over limits  $b-2\sigma$  to  $b+2\sigma$ , where  $\sigma$  is the standard deviation of the sample curve.

There are several ways this calculation can be simplified. Overlap can be determined for curves of unit area; then actual areas can be introduced. The desired integration can be resolved into two integrals of the normal distribution function for which there are convenient calculation programs and tables. An example would be Program 15 in Texas Instruments Program Manual ST1, 1975. Texas Instruments, Inc., Dallas, Texas 75222.

$$\frac{1}{\sqrt{2\pi}\sigma_c} \int_{b-2\sigma_s}^{b+2\sigma_s} e^{-\frac{t^2}{2\sigma_c^2}} dt = \frac{1}{\sqrt{2\pi}} \int_{\frac{b-2\sigma_s}{\sigma_c}}^{\frac{b+2\sigma_s}{\sigma_c}} e^{-\frac{x^2}{2}} dx = \frac{1}{\sqrt{2\pi}} \int_{\frac{b+2\sigma_s}{\sigma_c}}^{\frac{b-2\sigma_s}{\sigma_c}} e^{-\frac{x^2}{2}} dx.$$

The following calculation steps are required:

1.  $2\sigma_s = t_s/\sqrt{2 \ln 2}$
2.  $\sigma_c = t_c/2\sqrt{2 \ln 2}$
3.  $x_1 = (b-2\sigma_s)/\sigma_c$
4.  $x_2 = (b+2\sigma_s)/\sigma_c$
5.  $Q(x_1) = \frac{1}{\sqrt{2\pi}} \int_{x_1}^{\infty} e^{-\frac{x^2}{2}} dx$
6.  $Q(x_2) = \frac{1}{\sqrt{2\pi}} \int_{x_2}^{\infty} e^{-\frac{x^2}{2}} dx$
7.  $I_o = Q(x_1) - Q(x_2)$
8.  $A_o = I_o A_c / A_s$
9. Percentage overlap =  $A_o \times 100$ .

where

- $A_s$  = The area of the sample peak of interest determined by electronic integration, or by the formula  $A_s = h_s t_s$ .
- $A_c$  = The area of the contaminant peak, determined in the same manner as  $A_s$ .
- $b$  = The distance on the chromatographic chart that separates the maxima of the two peaks.
- $h_s$  = The peak height of the sample compound of interest, measured from the average value of the baseline to the maximum of the curve.
- $t_s$  = The width of the sample peak of interest at 1/2 of peak height.
- $t_c$  = The width of the contaminant peak at 1/2 of peak height.
- $\sigma_s$  = The standard deviation of the sample compound of interest elution curve.
- $\sigma_c$  = The standard deviation of the contaminant elution curve.
- $Q(x_1)$  = The integral of the normal distribution function from  $x_1$  to infinity.
- $Q(x_2)$  = The integral of the normal distribution function from  $x_2$  to infinity.
- $I_o$  = The overlap integral.
- $A_o$  = The area overlap fraction.

\*In most instances,  $Q(x_2)$  is very small and may be neglected.

In judging the suitability of alternate gas chromatographic columns, or the effects of altering chromatographic conditions, one can employ the area overlap as the resolution parameter with a specific maximum permissible value.

The use of Gaussian functions to describe chromatographic elution curves is widespread. However, some elution curves are highly asymmetric. In those cases where the sample peak is followed by a contaminant that has a leading edge that rises sharply but the curve then tails off, it may be possible to define an effective width for  $t_c$  as "twice the distance from the leading edge to a perpendicular line through the maxim of the contaminant curve, measured along a perpendicular bisection of that line."

#### Supplement B—Procedure for Field Auditing GC Analysis

Responsibilities of audit supervisor and analyst at the source sampling site include the following:

A. Check that audit cylinders are stored in a safe location both before and after the audit to prevent vandalism of same.

B. At the beginning and conclusion of the audit, record each cylinder number and cylinder pressure. Never analyze an audit cylinder when the pressure drops below 200 psi.

C. During the audit, the analyst is to perform a minimum of two consecutive analyses of each audit cylinder gas. The audit must be conducted to coincide with the analysis of source test samples. Normally, it will be conducted immediately after the GC calibration and prior to the sample analyses.

D. At the end of audit analyses, the audit supervisor requests the calculated concentrations from the analyst and then compares the results with the actual audit concentrations. If each measured concentration agrees with the respective actual concentration within  $\pm 10$  percent, he then directs the analyst to begin the analysis of source samples. Audit supervisor judgment and/or supervisory policy determine course of action with agreement is not within  $\pm 10$  percent. Where a consistent bias in excess of 10 percent is found, it may be possible to proceed with the sample analyses, with a corrective factor to be applied to the results at a later time. However, every attempt should be made to locate the cause of the discrepancy, as it may be misleading. The audit supervisor is to record each cylinder number, cylinder pressure (at the end of the audit), and all calculated concentrations. The individual being audited must not under any circumstance be told the actual audit concentrations until the calculated concentrations have been submitted to the audit supervisor.

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Office of Air Quality Planning and Standards  
Research Triangle Park, North Carolina 27711

DATE: 4/21/81

SUBJECT: Source Test Report

FROM: J. E. McCarley, Chief, Field Testing Section,  
Emission Measurement Branch, ESED (MD-13)

TO: See Below

The enclosed final source test report is submitted for your information. Any questions regarding the test should be directed to the Project Officer (telephone: 8/629-5543). Additional copies of this report are available from the ERC Library, Research Triangle Park, North Carolina 27711.

Industry: Benzene

Process: Coke Oven By-Product

Company: Wheeling-Pittsburgh Steel Corporation

Location: Monessen, PA

Project Report Number: 80-BYC-3

Project Officer: Dan Bivins

Enclosure

Addressees:

Ken Knapp, ESRL (MD-46)

Arch MacQueen, MDAD (MD-14)

Rodney Midgett, EMSL (MD-77)

Mark S. Siegler, DSSE (MD-EN-341)

Director, Air & Hazardous Materials Division, Region III

(copy enclosed for State agency)

Bob Kilgore, EPA Library Services (MD-35)