SET 1957 07 0181

BENZENE SAMPLING PROGRAM AT COKE BY-PRODUCT RECOVERY PLANTS: BETHLEHEM STEEL CORPORATION, BURNS HARBOR, INDIANA

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

Prepared For:

Mr. Daniel Bivins
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Emission Measurement Branch, ESED, MD-13
Research Triangle Park, North Carolina 27711

March 1981

SCOTT ENVIRONMENTAL SERVICES
A Division Of
SCOTT ENVIRONMENTAL TECHNOLOGY, INC.
Plumsteadville, Pennsylvania 18949

Scott Environmental Technology Inc.

TABLE OF CONTENTS

1.0 INTRODUCTION

Scott Environmental Services, a division of Scott Environmental Technology, Inc., conducted a testing program at Bethlehem Steel Corporation in Burns Harbor, Indiana to determine benzene emissions from two sources in the coke by-product recovery plant. The work was performed for the United States Environmental Protection Agency under Contract No. 68-02-2813, Work Assignment 48. This plant was one of seven plants visited to collect data for a possible National Emission Standard for Hazardous Air Pollutants for benzene.

Sampling was conducted at Burns Harbor on September 23rd and 24th, 1980. Integrated air samples and liquid samples for benzene analysis were collected from the tar decanter and the tar dehydrator.

2.0 SUMMARY OF RESULTS

Process	Benzene Emission Rate	
	lb/hr	kg/hr
Tar Decanter	9.73	4.42
Tar Dehydrator	3.99	1.81

3.0 RESULTS AND DISCUSSION

3.1 TAR DEHYDRATOR

The dehydrator holds tar from the decanter at an elevated temperature for dewatering prior to pumping it to tar storage. Benzene contained in the tar will potentially be removed with the water.

Three Method 110 tests were run on the tar dehydrator with an average result of 3.99 lb/hr benzene. The test results are summarized in Table 3-1. The tests were conducted at one of the three vent stacks on the dehydrator. (See Figure 6-1). The other two vents were blocked while the sampling runs were being conducted.

Liquid samples were collected at the dehydrator outlet from a pump. The liquid samples had a temperature of 162°F and an average benzene concentration of 1990 ppm.

All stack flowrates 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 in. Hg. (2½% moisture). Example calculations are shown in Appendix A.

TABLE 3-1

TAR DEHYDRATOR DATA SUMMARY

Process Tar Dehydrator

Stack Diameter 4"

Plant Bethlehem Steel, Burns Harbor, IN

Stack Area 0.087 ft^2

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	9/24/80	1005-1035	149	29.5	710	61	38	8615.2	3.97
2	9/24/80	1100-1130	152	29.5	680	59	36	9968.0	4.30
3	9/24/80	1202-1232	158	29.5	710	62	35	8816.4	3.69
								Avg.	3.99

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

Liquid Sample Data

Sample Location	Date	Time	Sample Temp (°F)	Benzene Concentration (ppm by weight)
Tar Dehydrator Outlet	9/23/80	1420	162	1956
	9/23/80	1420	162	1834
	9/23/80	1420	162	2171
			Avg.	1987 ppm

3.2 TAR DECANTER

The tar decanter tested at Burns Harbor (Decanter B) was receiving tar from the primary cooler. There are three vent stacks on the decanter, which were sampled simultaneously. (See Figure 6-2).

The results of the testing are shown in Table 3-2. The average benzene emission rate from the decanter (total of all three stacks) was measured to be 9.73 lb/hr. Vent A was nearest the inlet and had the highest measured benzene concentrations, and Vent C, nearest the outlet, had the lowest.

Liquid sample data is given in Table 3-3. Samples were dipped from the hatchway in the center of the decanter and from the weir outlet at the end of the decanter. Average benzene concentrations were 92 ppm and 4506 ppm respectively.

TABLE 3-2

TAR DECANTER DATA SUMMARY

Process Tar Decanter B

Plant Bethlehem Steel, Burns Harbor, IN

	Vent A	Vent B	Vent C
Stack Diameter	5 1/2"	9 3/4"	5 1/2"
Stack Area	0.165 ft^2	0.518 ft^2	0.165 ft^2

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)
Vent A									
1	9/23/80	1020-1050	109	29.47	406	67	58	4760.0	3.34
2	9/23/80	1150-1220	101	29.47	380	63	55	3198.7	2.14
3	9/23/80	1407-1437	101	29.47	475	78	69	4701.6	3.94
Vent B									
1	9/23/80	1020-1050	108	29.47	420	218	188	1819.0	4.14
2	9/23/80	1150-1220	106	29.47	440	228	197	2252.2	5.38
3	9/23/80	1407-1437	107	29.47	620	321	278	2350.8	7.91
Vent C									
1	9/23/80	1020-1050	107	29.47	415	68	59	850.0	0.61
2	9/23/80	1150-1220	104	29.47	390	64	56	1126.1	0.76
3	9/23/80	1407-1437	106	29.47	460	76	66	1207.7	0.96

Total Emission Rate (A + B + C)

Run 1 8.09 lb/hr

Run 2 8.28 lb/hr Avg. 9.73 lb/hr

Run 3 12.81 lb/hr

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

TABLE 3-3

TAR DECANTER LIQUID SAMPLE DATA

Sample Location	Date	Time	Sample Temp (°F)		Benzene Conc. (ppm by weight)
Dipped from center hatch (between Vents B and C)	9/23/80	1525	120		181.6
					58.1
					35.5
				Avg.	91.7
Weir Outlet (near Vent C)	9/23/80	1415	178		4387
					4637
					4495
				Avg.	4506

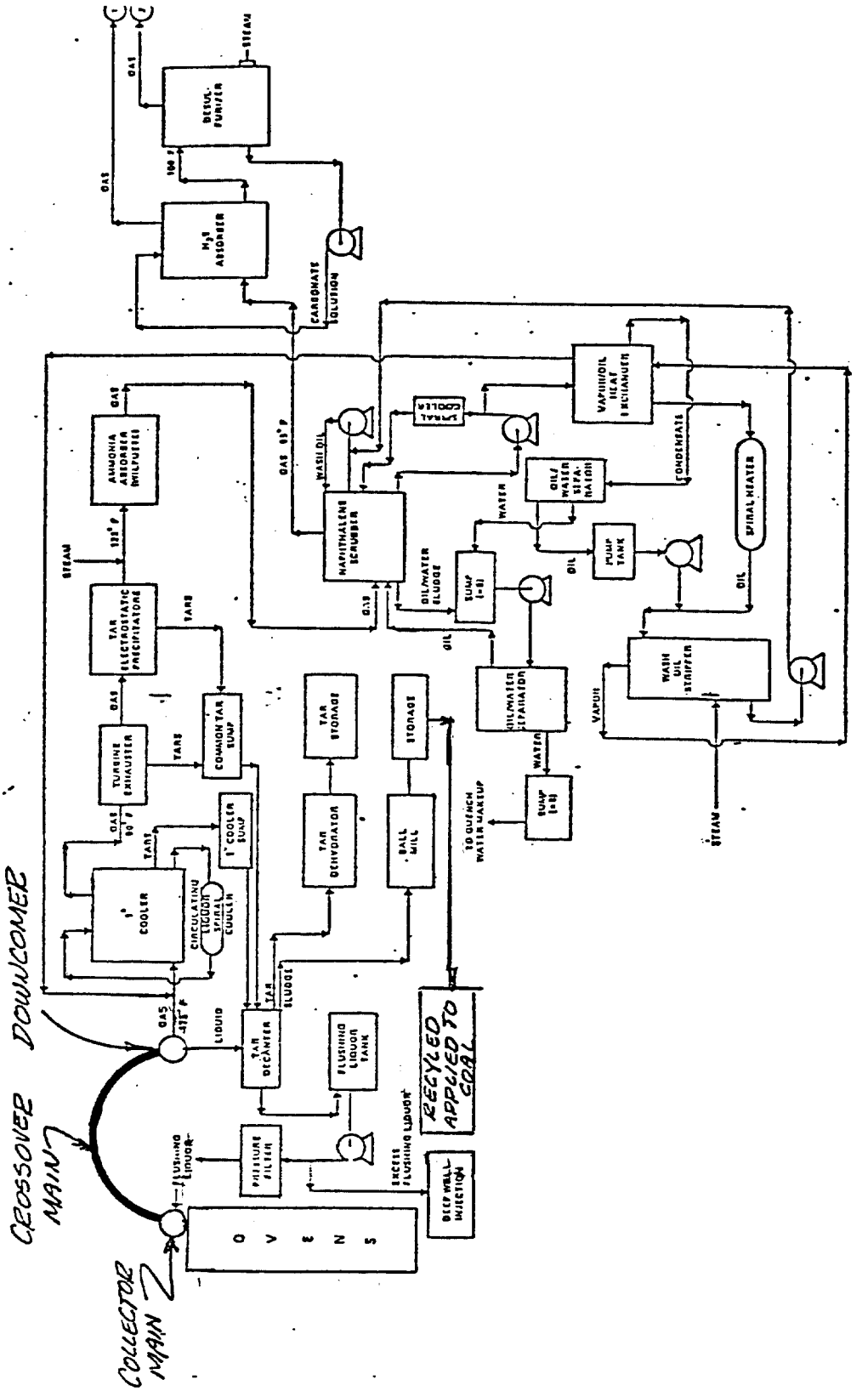
4.0 PROCESS DESCRIPTION

The processes used at Burns Harbor for recovery of coke oven gas are primary cooling, tar decanting and dehydrating, turbine exhausters, tar electrostatic precipitation, Wilputte semi-direct ammonia absorption, naphthalene scrubbing, and a hydrogen sulfide absorption. The desulfurization process is currently not in use at the plant. A process flow diagram of the gas and liquid streams is depicted in Figure 4-1.

The gas leaving the ovens is collected in the collecting main where it is sprayed with flushing liquor for initial cooling. The gas and flushing liquor leave the battery area and are transported from the collecting main through cross-over mains into the suction main and 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 and the gas continues to the primary cooler.

The three tar decanters separate the liquor into tar and water layers and sludge. Inputs to the three tar decanters are mainly the flushing liquor from the downcomer, but the middle decanter receives effluents from the primary cooler sump and common tar sump for the exhausters and electrostatic precipitators. The tar layer at 75°C is sent to the tar dehydrator where the tar is held at 65°C for reduction of the moisture content from 10-12 percent to 2-3 percent. There are steam coils on the tar dehydrator but at the present time they are disconnected. From the tar dehydrator, the tar is pumped to final storage before sale. From the tar decanters, the water layer is discharged at 68°C to a flushing liquor tank where it is stored before being pumped either through a pressure filter to the collecting main for flushing or to cooling and settling basins before deep

FIGURE 4-1



Scott Environmental Technology Inc.

PROCESS FLOW DIAGRAM OF THE COKE OVEN BY-PRODUCT RECOVERY PLANT AT BETHLEHEM STEEL, BURNS HARBOR, IN

well injection. The sludge is scraped off the bottom of the decanter and transferred to a ball mill where it is crushed and heated to 86°C to reduce the viscosity of the sludge before it is pumped to storage. From storage, the tar sludge is mixed with coal for charging in the coke ovens.

The gas stream at the downcomer goes to the primary coolers at approximately 80°C. Gas from the wash oil strippers is combined with the main gas stream before entering the primary coolers. The three primary coolers are direct contactors, without packing, of the water and the gas. The water is pumped to the primary coolers at 3.5×10^{-2} m^3/s (500 gpm). The water is circulated within the primary coolers twice before indirect cooling in the circulating liquor spiral coolers. Tars are pumped from the primary cooler sump at 1.3×10^{-3} m^3/s (20 gpm) to the tar decanters. The gas stream leaves the primary coolers at approximately 32°C.

From the primary coolers, the gas enters the turbine exhausters where the pressure changes from vacuum to positive. The three turbine exhausters provide the motive power for the by-product recovery operations. Some tars are separated in the exhauster and drained to the common tar sump before pumping to the tar decanter. The gas leaving the exhausters is approximately 38°C due to heat of compression.

The gas from the exhausters enters the tar electrostatic precipitators where additional tar is separated from the gas and discharged to the common tar sump from the seal pots on each electrostatic preceipitator. There are four electrostatic precipitators, but only three are in operation at a time.

The gas stream leaving the electrostatic precipitators is injected with steam to elevate the temperature to 50°C. In the ammonia absorber, the

gas is sprayed with sulfuric acid in a Wilputte system producing ammonium sulfate. In this system, the spray is not saturated with salt and a separate crystalizer is operated by evaporative cooling under subatmospheric pressure. Water vapor with entrained impurities passes through steam ejectors in a cascade. Barometric condensers exhaust the hot condensate to a sump. The blowdown from the system is discharged to the No. 1 battery quench station as make up water.

The gas then enters the naphthalene scrubbers at approximately 55-60°C due to the exothermic heat of reaction in the ammonia absorber. Two of three naphthalene scrubbers are operated in parallel. The remaining naphthalene scrubber serves as a spare. The gas stream leaving the naphthalene scrubbers is approximately 35°C before entering the hydrogen sulfide absorber. Part of the wash oil, rich in naphthalene, is cooled in an indirect spiral cooler, and part 2.5×10^{-3} m^3/s (40 gpm) is sent to a stripping operation. A light oil scrubber would operate at $7.6 \times 10^{-2} \times m^3/s$ (1200 gpm) as indicated by the plant personnel. The reason for the lower rate is that the plant only desires to remove the naphthalene from the gas; the light oil is not recovered but burned with the clean coke oven gas at various plant combustion facilities. A higher rate of stripping would facilitate removal of the light oil by the wash oil in the naphthalene scrubber.

The rich wash oil bleed stream sent to the wash oil stripper passes through a vapor/oil heat exchanger and spiral heater before entering the wash oil stripper. Condensate from the vapor/oil heat exchanger is drained to an oil/water separator. The oil from the oil/water separator is drained to a pump tank and then pumped to the wash oil stripper. The

water from the oil/water separator is discharged to a sump (No. 5). In the wash oil stripper, steam is injected and naphthalene rich vapors leave the top of the stripper at approximately 155°C and are piped to the gas stream before the primary coolers. The stripped lean wash oil returns through the vapor/oil heat exchanger to the suction line of the top re-spray pump of the naphthalene scrubber.

An oil/water sludge layer accumulates in the naphthalene scrubber and is drained to sump No. 5. The oil and water in sump No. 5 are pumped to an oil/water separator. The separated oil is returned to the wash oil layer in the napthalene scrubber and the water layer is pumped to another sump (No. 8). The water in this sump is then used as makeup water for quenching of the coke.

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.

---

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

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:

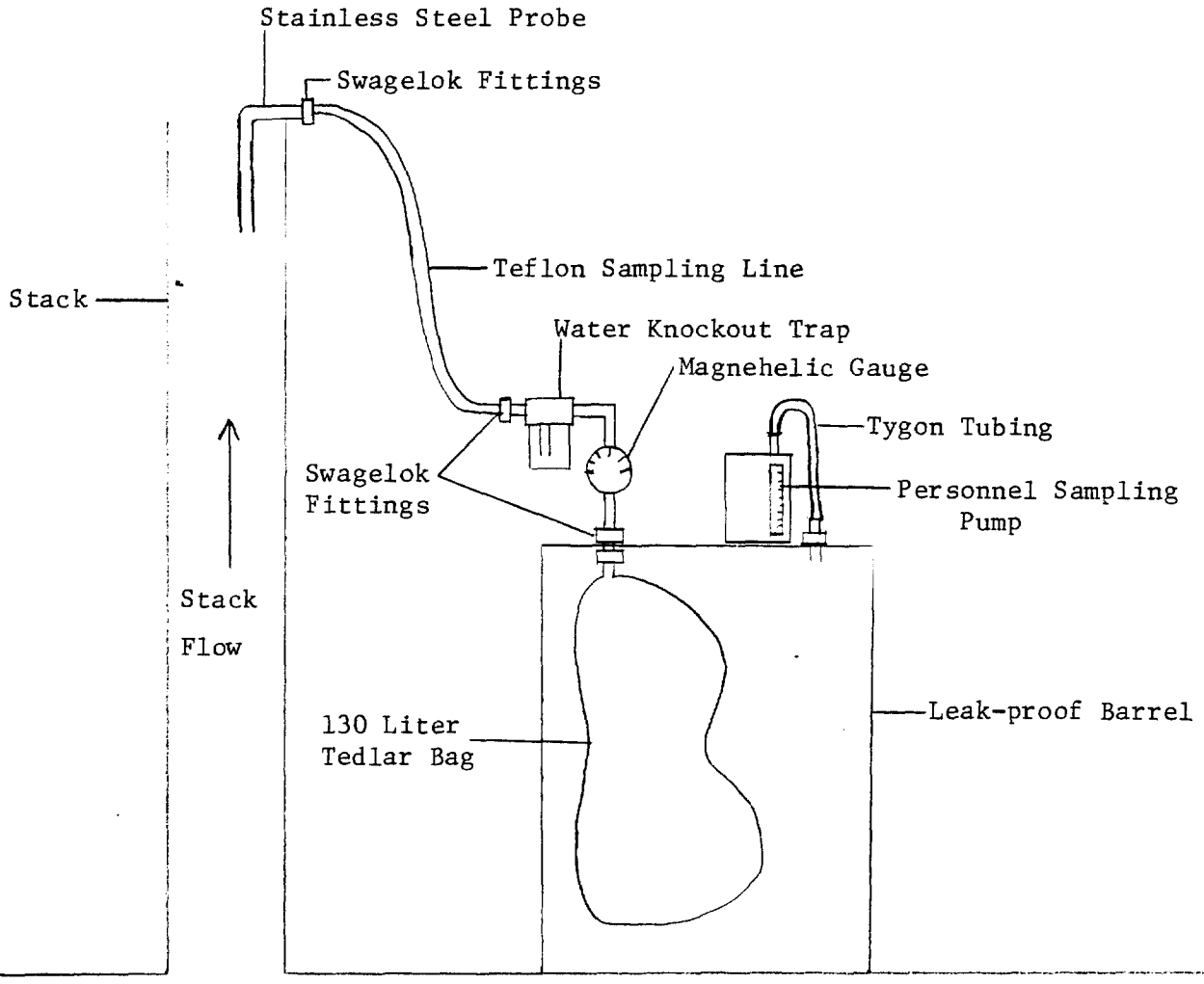
If any condensate was collected in the trap or sample line, it was measured and saved for analysis. The probe, line and trap were then washed with propylene carbonate, which was also saved for analysis. Any benzene found in these washes and water catches was added to the total found in the sample bag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



Scott Environmental Technology Inc.

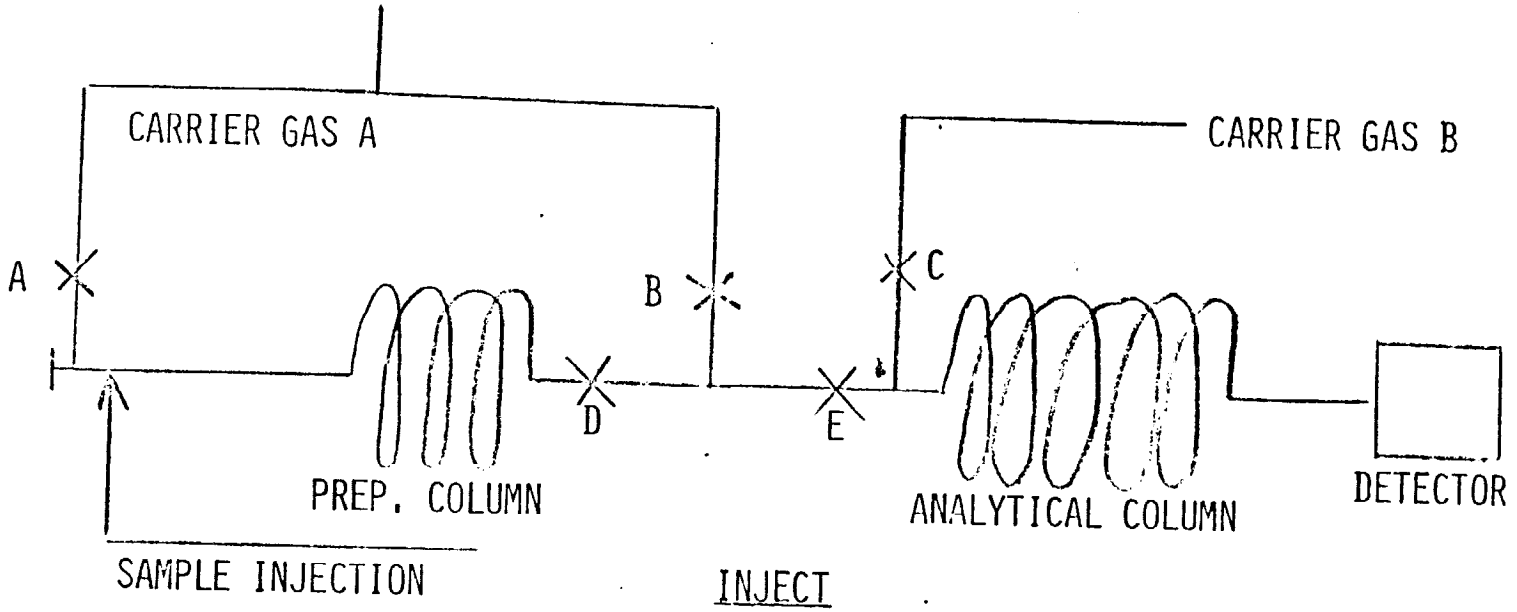
MODIFIED METHOD 110 SAMPLING TRAIN

5.2 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%.

5.3 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 a 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.



INJECT

A, D, E OPEN

B, C CLOSED

BACKFLUSH

A, E CLOSED

B, C, D OPEN

FIGURE 5-2

GC COLUMN CONFIGURATION WITH BACKFLUSH

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 injection. 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

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.

6.0 FIELD SAMPLING PROCEDURES

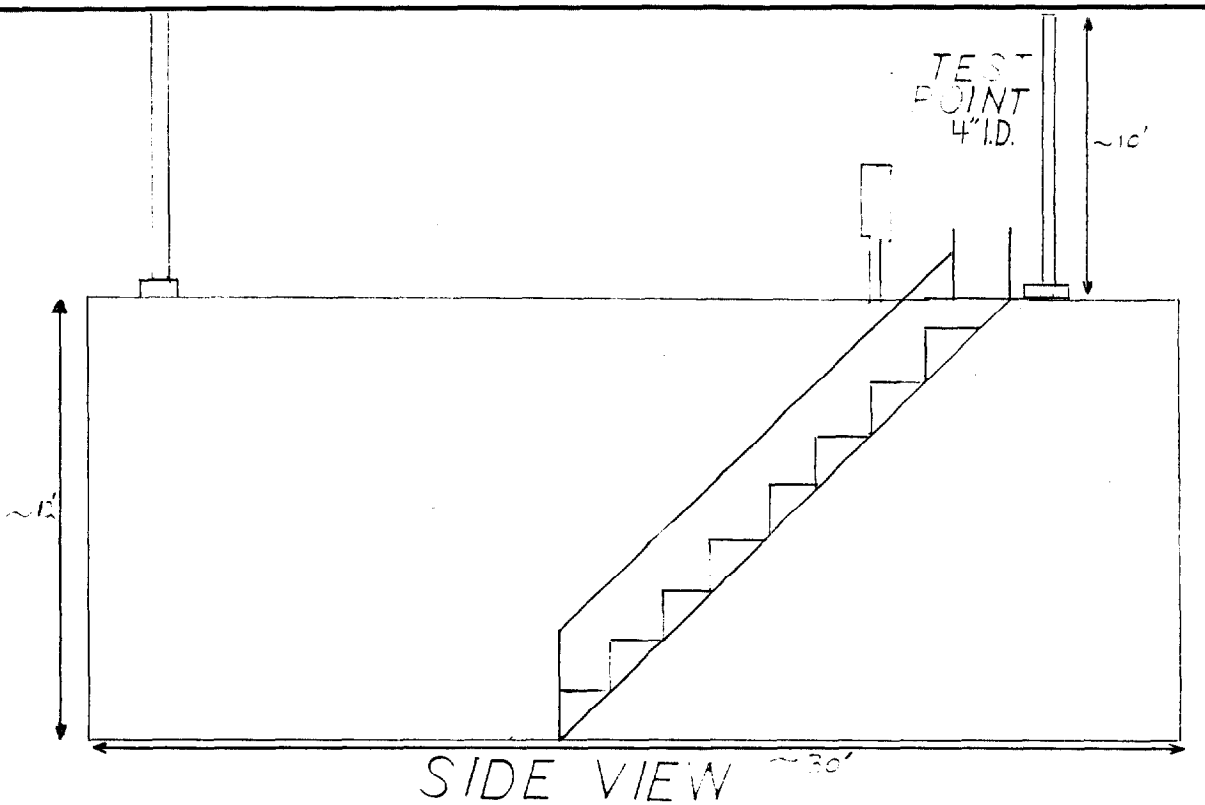
6.1 TAR DEHYDRATOR

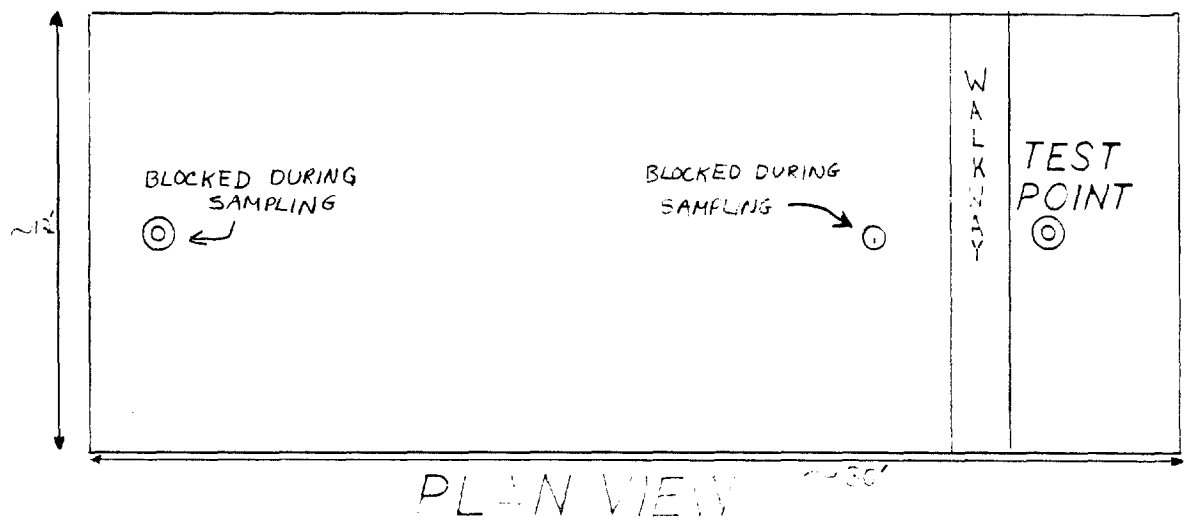
Three Method 110 test were conducted on the tar dehydrator. As shown in Figure 6-1, the dehydrator has three vents, which are normally all open. Sampling was conducted at the end vent nearest the stairs as marked on the diagram, and the other two vents were blocked off during testing. Ideally all three vents should have been sampled simultaneously, but the end vent furthest from the walkway was not safely accessible for sampling. Since only one vent was sampled, the calculated mass emission rate of 4 lb/hr is possibly low. The maximum emission rate could be as high as 12 lb/hr (3 vents x 4 lb/hr) although this is not considered likely because field observations revealed that no steam plume emanated from the test vent until the center vent was blocked, since the center vent was lower and of larger diameter, and located within 5 feet of the test vent. The vent on the far end had an observable plume before it was blocked.

Also, the prime driving force of the emissions is the volatilization of organics in the heated tar, which would not be affected by closing the vents. The only change would be the elimination of breathing losses through those two vents. For these reasons, it is estimated that the actual emission rate is on the order of 6 to 8 lb/hr maximum.

The moisture content of the stream was about 30%, i.e. saturated, as determined by the volume of condensate collected in the water trap and the sample volume in the bag.

Liquid samples were collected from a pump at ground level at the dehydrator outlet.





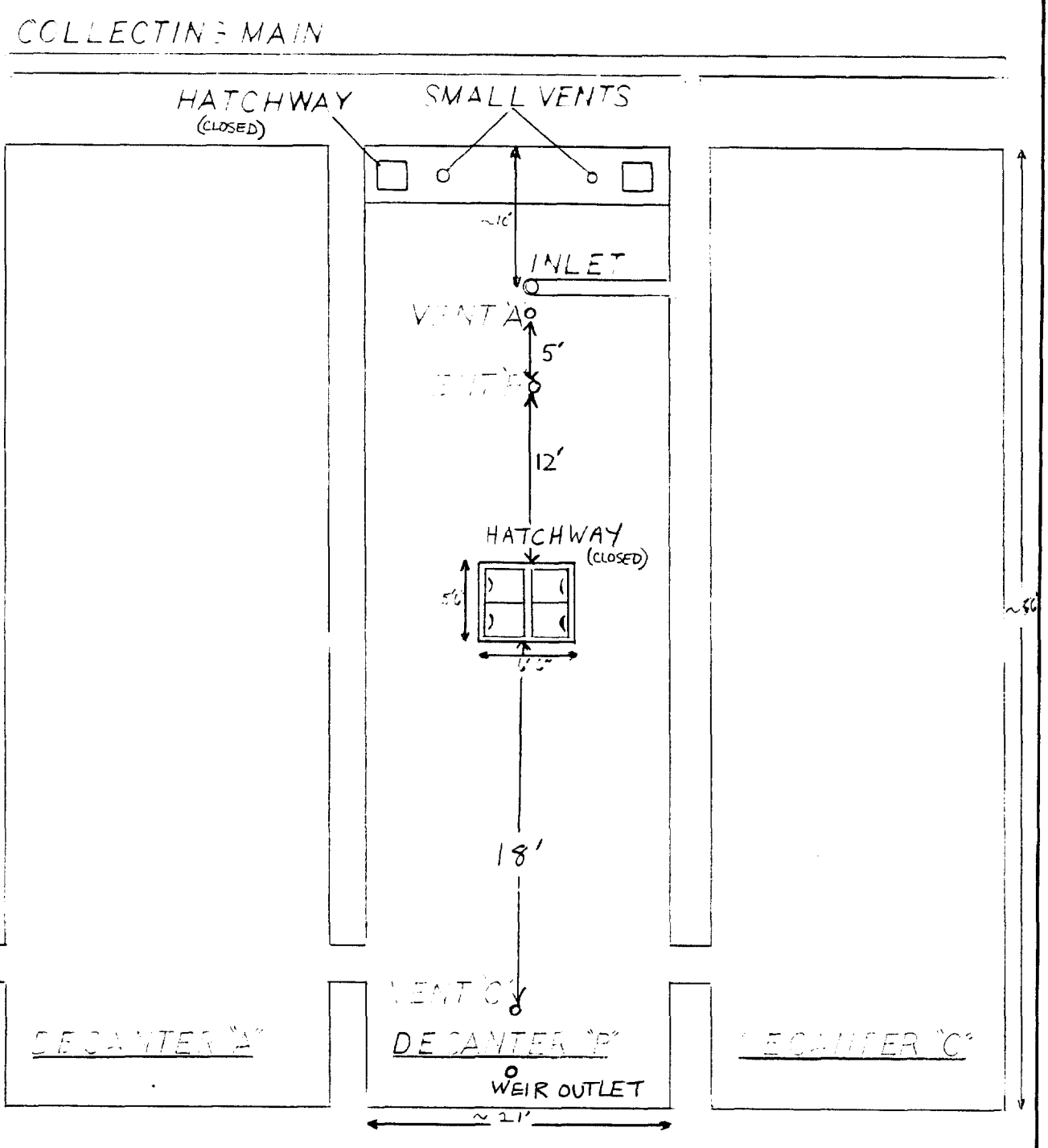
Scott Environmental Technology Inc.

FIGURE 6-1 TAR DEHYDRATOR

6.2 TAR DECANTER

Three sets of simultaneous Method 110 tests were conducted on the three vent stacks on the tar decanter. Figure 6-2 depicts the decanter and shows the locations of the vents and the hatchway and weir outlet where liquid samples were collected. All hatchways were closed during sampling.

The tests were run according to the revised Method 110 procedure outlined in Section 5.1, except that one of the sampling trains did not include the magnehelic gauge because only two were available. No problems were encountered with the sample line plugging.



VENT A : 5½" I.D.
VENT B : 9¾" I.D.
VENT C : 5½" I.D.

LIQUID LEVEL ~ 2 ft. below deck
VENTS A, B, C ~ 10-12 ft. high

Scott Environmental Technology Inc.

FIGURE 6-2 TAR DECANTER "B"

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 ±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.

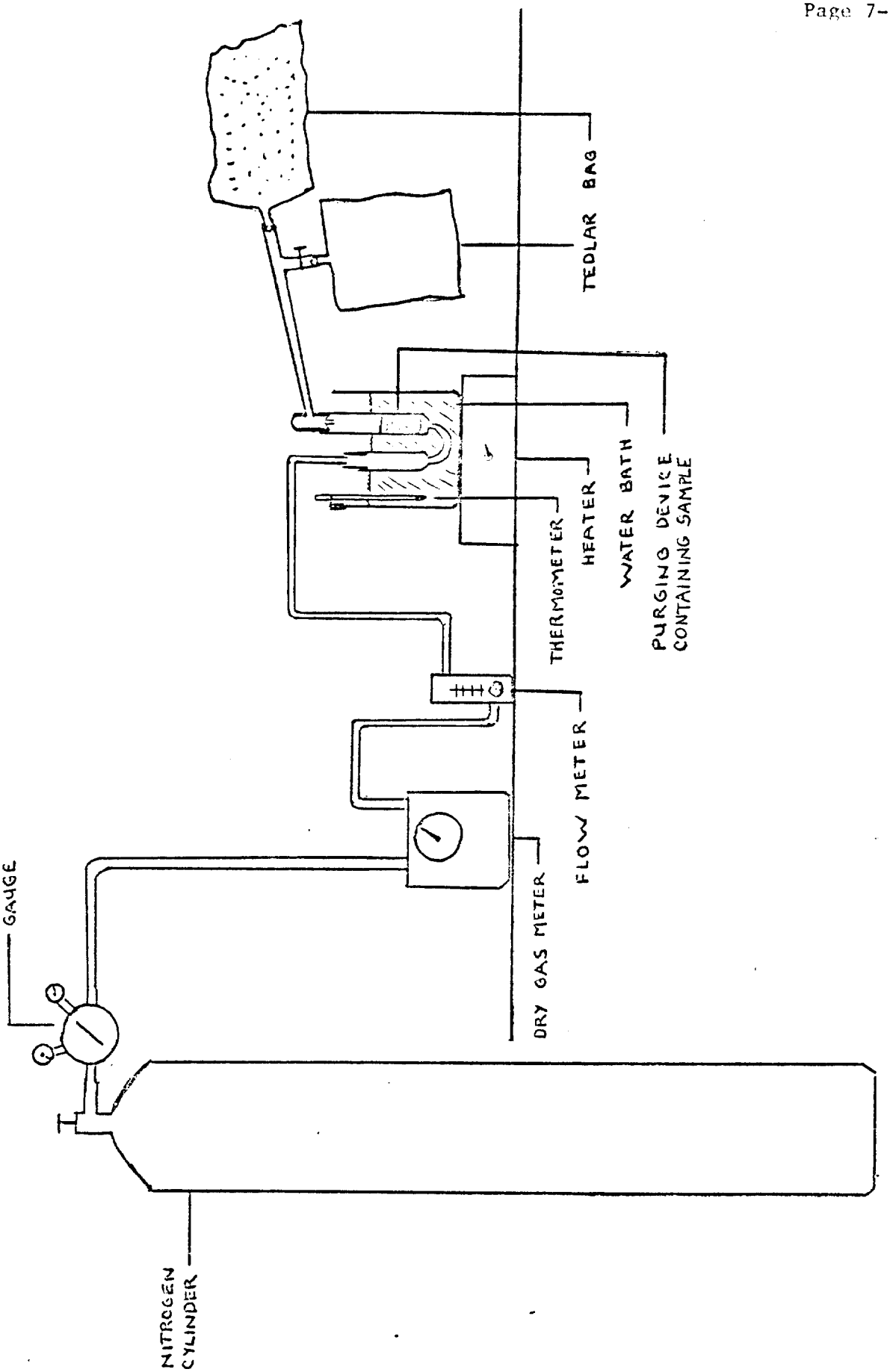


FIGURE 7-1 PURGE AND TRAP METHOD EQUIPMENT SET-UP

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.

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 ±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. Calculation of percent moisture from water catch and bag volume

Example: tar dehydrator, Run 1

Water trap catch volume: 13 ml

Tedlar bag volume (gas sample): 45.43 liters

Gaseous volume of collected water, standard conditions:

$$13 \text{ ml} \times \frac{1 \text{ gm}}{\text{ml}} \times \frac{1 \text{ mole}}{18 \text{ gm}} \times \frac{24.15 \text{ l}}{\text{mole}} = 17.44 \text{ liters}$$

Percent moisture:

$$\frac{17.44}{17.44 + 45.43} \times 100 = 27.74\%$$

2. Flow rate at standard conditions (saturated at 68°F, 29.92 inches Hg)

A. Correction for temperature and pressure:

$$\text{Flow Rate (STP)} = \text{Flow Rate (source)} \times \frac{528°R}{T(°F) + 460} \times \frac{P_{bar}(\text{in. Hg})}{29.92}$$

Example: Tar dehydrator, Run 1

$$\text{Flow Rate(STP)} = 62 \text{ cfm} \times \frac{528}{149 + 460} \times \frac{29.5}{29.92} = 53 \text{ cfm}$$

B. Correction for moisture:

Percent moisture (stack conditions) = 27.74%

Percent moisture (saturated at 68°F) = 2.5%

Flow Rate (dry) = Flow Rate(STP) x (100 - % Moisture)/100

= 53 cfm x (100 - 27.74)/100

= 38 cfm

Flow Rate (saturated at 68°F) = Flow Rate (dry) x 1.025

= 38 cfm x 1.025

= 39 cfm

3. Calculation of mass emission rate

Example: Tar dehydrator, Run 1

Flow Rate (standard conditions) = 39 cfm

Benzene concentration: 8615.2 ppm

$$\frac{39\ ft^3}{min} \times \frac{28.32\ l}{ft^3} \times \frac{60\ min}{hr} \times \frac{8615.2}{10^6} \times \frac{78\ g}{mole} \times \frac{1\ mole}{24.15\ l} \times \frac{1\ lb}{454\ g} = 4.06\ lb/hr$$

APPENDIX B

FIELD DATA SHEETS

SCOTT ENVIRONMENTAL TECHNOLOGY, INC.

PROJECT 1957 07 0181 METHOD 110 DATA SHEET

PLANT: Burns Harbor DATE: 9/24/80

PROCESS: Tar dehydrator AMBIENT TEMPERATURE:

PROCESS NOTES: end vent BAROMETRIC PRESSURE:

TEDLAR BAG NUMBER:

RUN 1 BAG A Can 4

TIME	STACK TEMP	GAS VELOCITY	PUMP FLOWRATE
10:05 0	148 °F	900 FPM	
5	148	900	13 ml. water catch
10	150	700	bag volume 45.43 l
15	149	640	
20	152	560	
25	148	600	
30	149	650	
	RUN 2	BAG E	
11:00 0	153 °F	620 FPM	
5	152	680	15 ml water catch
10	151	700	
15	153	630	bag volume 45.68 l
20	154	610	
25	152	700	
30	152	750	
	RUN 3		
12:02 0	154 °F	660 FPM	13 ml H_2O
5	157 °F	950	
10	158	640	bag volume 31.50 l
15	157	650	
20	159	670	
25	161	720	
30	157	700	

SCOTT ENVIRONMENTAL TECHNOLOGY, INC.

PROJECT 1957 07 0181 METHOD 110 DATA SHEET

PLANT: Burns harbor DATE: 9/23/80

PROCESS: Tardecanter AMBIENT TEMPERATURE:

PROCESS NOTES: BAROMETRIC PRESSURE:

TEDLAR BAG NUMBER:

Stack A (near collecting main) RUN 1, CAN 1, BAG B

TIME	STACK TEMP	GAS VELOCITY	PUMP FLOWRATE
5	111 °F	440 fpm	
11	105 °F	400 fpm	
20	106 °F	390 fpm	
26	111 °F	400	
31	110	380	
off at 35			
	RUN 2	BAG G	
4	102 °F	330 fpm	
9	102	320	
15	100	320	
21	100	300	
27	101	310	
34	102	520	
	RUN 3	BAG E	
4	102 °F	350 fpm	
9	105	350	
15	100	780	
20	100	500	
26	101	420	
30	99	400	

SCOTT ENVIRONMENTAL TECHNOLOGY, INC.

PROJECT 1957 07 0181 METHOD 110 DATA SHEET

PLANT: Burns Harbor DATE: 9/23

PROCESS: Tar decanter AMBIENT TEMPERATURE:

PROCESS NOTES: BAROMETRIC PRESSURE: 29.47

Stack B TEDLAR BAG NUMBER:

RUN 1, CAN 3, BAG 4.

TIME	STACK TEMP	GAS VELOCITY	PUMP FLOWRATE
3	108 °F	340 fpm	
9	103 °F	440 fpm	
18	104 °F	430 fpm	
24	113 °F	380	
30	112	460	
off at 33			
0	RUN 2	BAG 1	
2	104 °F	350 fpm	
7	113	370	
14	111	380	
20	102	380	
26	105	390	
32	103	700 (irregular)	
	RUN 3	BAG 3	
2	106 °F	380 fpm	
7	108	900	
13	107	680	
18	107	550	
24	107	800	
29	107	460	

SCOTT ENVIRONMENTAL TECHNOLOGY, INC.

PROJECT 1957 07 0181 METHOD 110 DATA SHEET

PLANT: Burns Harbor DATE: 9/23/80

PROCESS: Tar decanter AMBIENT TEMPERATURE: ~60°F

PROCESS NOTES: BAROMETRIC PRESSURE: 29.47

Stack C TEDLAR BAG NUMBER:

RUN 1, CAN 4, BAG 12

TIME	STACK TEMP	GAS VELOCITY	PUMP FLOWRATE
10:20 0	106 °F	425 fpm	
7	106	430	
14	113	420	
22	105	380	
28	106	400	
off at 33			
	RUN 2 BAG 11		
11.50 0	111 °F	390 fpm	
5	104 °F	340	
12	102	380	
18	102	350	
24	101	400	
29	103	400	
	RUN 3 BAG 7		
2:07 0	109 °F	450 FPM	
5	106	420	
11	105	300	
16	105	1500	
22	105	550	
27	105	500	
31 off			

PROJECT 1957 07 0181

SAMPLE DATA

Plant Burns Harbor Process TAR decanter Date 9/23/80

Sample No. TAR Decanter #1,2,3 Time Sampled 3:25

Sample Type: (Liquid) Air

Sample Temperature 120 °F

Ambient Temperature ~60 °F

Description of Sampling Location: dipped from hatchway in center of tank

---

Sample No. Tar decanter weir (outlet) #1,2,3 Time Sampled 2:15

Sample Type: (Liquid) Air

Sample Temperature 178 °F

Ambient Temperature

Description of Sampling Location: dipped from weir at Decanter outlet

---

Sample No. Tar dehydrator outlet Time Sampled 2:20

Sample Type: (Liquid) Air

Sample Temperature 162 °F

Ambient Temperature

Description of Sampling Location: taken from pump at tank outlet

APPENDIX C

LABORATORY DATA SHEETS

Scott Environmental Technology Inc.

CHROMATOGRAPHIC ANALYSIS LOG Bethlehem Steel, Burns Harbor

Project No. 1957 07 0181 Date 9/23/80 Analyst TB

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	122.5 ppm ¢ Std 32×10^2	41	2.99		
	Cal Temp 150°C				
	100l Bag Background @ 8×10^2		0.75		
	Bag #4	3.5			
	Bag #12	3			
	Bag #1	ND			
	Bag #11	1.5			
	Bag G	ND			
	Bag #7	ND			
	Bag #3	1			
	Bag A	2			
	122.5 ppm ¢ Std 32×10^2	40.5			

SET 1957 07 0181

Scott Environmental Technology Inc.

CHROMATOGRAPHIC ANALYSIS LOG

Burns Harbor, Bethlehem Steel

Project No. 1957 07 0181 Date 9/23/80 Analyst TB

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	122.5 ppm ϕ Stl $.32 \times 10^2$ Col Temp 100°C No BF	26.5	454		
	122.5 ppm ϕ Stl 2min BF	27.5	~~4.85~~		
	Ton Deconter Run# 1 256×10^2 Bag#4 Vent B	53.5	(4.25) 340	1819 ppm	~~3543~~ 54.91 l
	Ton Deconter Run# 1 256×10^2 Bag#12 Vent C	25	(4.25) 340	850 ppm	38.63 l.
	Ton Deconter Run# 1 1024×10^2 Bag B Vent A	35	(4.25) 136.0	<1760 ppm	27.36 l.
	122.5 ppm ϕ Stl 32×10^2	31	395 4.25		

SET 1957 07 0181

Scott Environmental Technology Inc.

CHROMATOGRAPHIC ANALYSIS LOG

Project No. 1957 07 0181 Date 9/23/80 Analyst JB

~~Tow Decanter~~ Bethlehem Steel, Bunn Harbor

SET 1957 07 0181

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	122.5 ppm @ Std 32×10^2	30	4.08		
	Tow Decanter Run #2				
	Bag #11 Vent C 256×10^2	34.5	32.64	1126.08 ppm	54.80 l
	Bag #1 Vent B 256×10^2	69	32.64	2252.16 ppm	27.36 l
	Bag G Vent A 1024×10^2	24.5	130.6	3198.72 ppm	27.10 l
	Std 122.5 ppm 32×10^2	30.5	4.08		

A G
B I
C II

Page C-4

Scott Environmental Technology Inc.

CHROMATOGRAPHIC ANALYSIS LOG Bethlehem Steel, Burns Harbor

Project No. 1957 07 0181 Date 9/23/80 Analyst TB

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	Top Decanter Run #3				
	Bag #7 Vent C 256×10^2	37	32.64	1207.68 ppm	52.02 l
	Bag #3 Vent B 256×10^2	72	32.64	2350.08 ppm	54.60 l
	Bag E Vent A 1024×10^2	36	130.6	4701.6	3432 l
	Std 122.5 ppm ϕ 32×10^2	30	4.08		

A 37
B 37
C 37

SET 1957 07 0181

Scott Environmental Technology Inc.

CHROMATOGRAPHIC ANALYSIS LOG Bethlehem Steel, Burn Harbor

Project No. 1957 07 0181 Date 9/24/80 Analyst TB

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	Std 122.5 ppm ϕ 32×10^2	27.5	4.45		~~Tar~~
	Tar Dehydrator				
	Run #1 Bag A 1024×10^2	60.5	142.40	8615.2 ppm	13cc catch 45.43l
	Bag E Background 32×10^2	NO			
	Bag G Background 32×10^2	NO			
	Std 122.5 ppm ϕ 32×10^2	28	4.45		
	Run #2 Bag E 1024×10^2	70	142.40	9968.0 ppm	15 cc catch 45.68l

SET 1957 07 0181

Scott Environmental Technology Inc.

CHROMATOGRAPHIC ANALYSIS LOG Bethlehem Steel, Burns Harbor

Project No. 1922 Date 9/24/80 Analyst TB

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	Std 122.5 ppm ϕ 32x10²	28	4.45		
	Tar Dehydration Runs 3 Bed G 1024/1.04	62	142.20	8816.4 ppm	13cc 31.80l
	Std 122.5 ppm ϕ 32x10²	28			

SET 1957 07 0181

APPENDIX D

EPA METHOD 110

(3) All [illegible] systems [illegible] shall [illegible] a minimum of one cycle of operation (sampling, analysis, and data recording) for each successive 15-minute period.

(c) 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 ±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])

§ 61.95 Recordkeeping requirements.

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

(b) Records are to be maintained 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 were the results of an adequate evaluation of known benzene desorption 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 confirmatory data through an alternate 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 (or other nonreactive material permitted), 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 shut-off checks (one [illegible] or 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 [illegible] 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, as 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 [illegible] sample valve. The chromatographic system shall be capable of producing [illegible] to a 1 ppm benzene that is at least as great as the average noise level. (Response is measured from the average value of the baseline to the maximum of the wave [illegible] while standard operating conditions are in use.)

BILLING CODE 6560-01-M

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

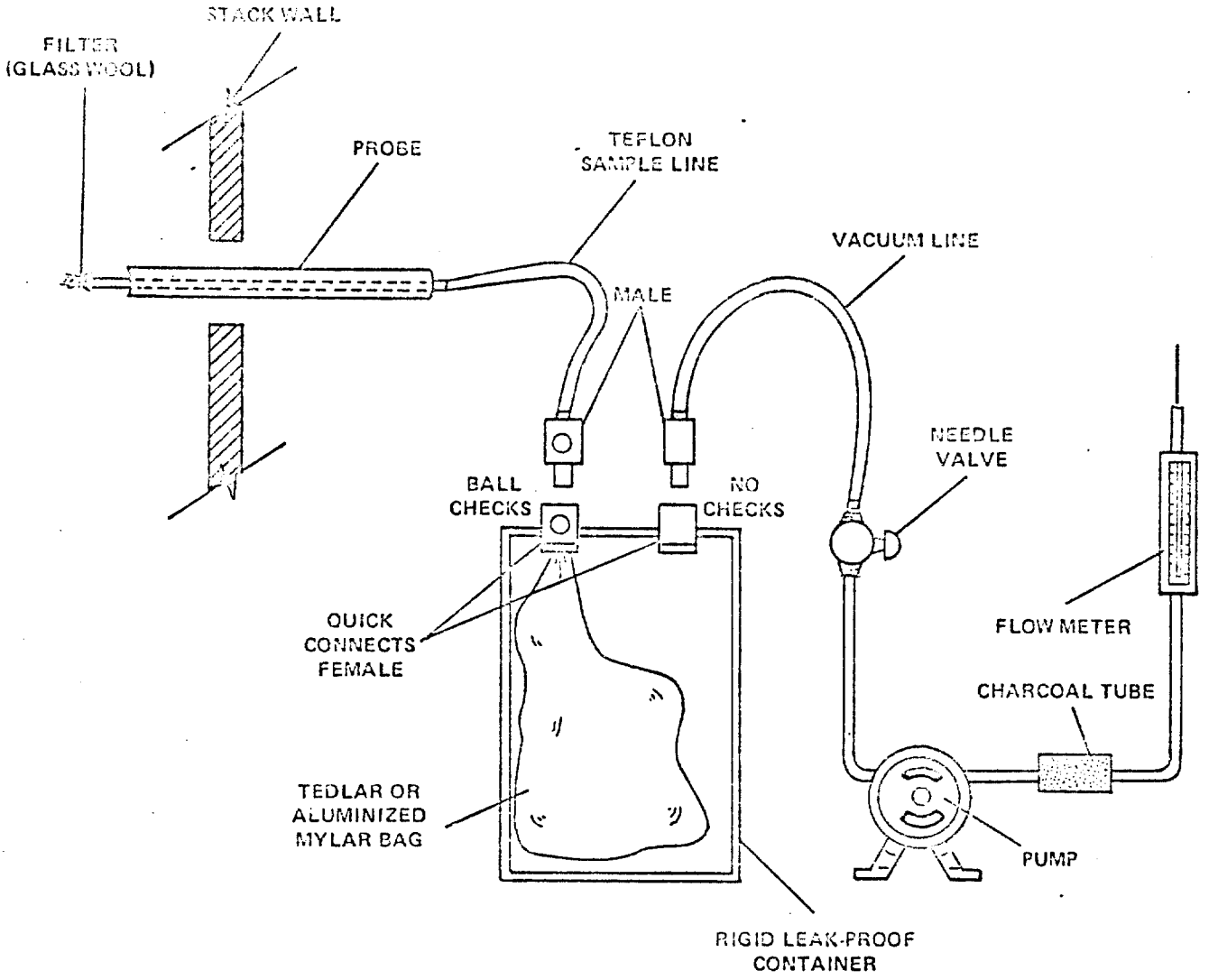


Figure 110-1. Integrated-bag sampling train. (Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.)

BILLING CODE 6560-01-C

4.3.2 Chromatographic Columns. Columns [illegible] below. [illegible] analyst may use other [illegible] resolution and [illegible] columns [illegible] standards are not [illegible] and he has [illegible] information confirming that [illegible] 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 mm Hg, 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 μL and 10 μL, gas tight, individually calibrated to dispense liquid benzene.

4.4.4 Dry Gas Meter, With Temperature and Pressure Gauges. Accurate to ±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 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 [illegible] 99 Mol Percent Pure. [illegible] 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 ±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 ±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 ±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 [illegible] to [illegible] ppm [illegible] available, the tester may obtain [illegible] 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 30 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-μL syringe to inject 10μL of 99+ percent benzene through the septum on top of the impinger. This gives a concentration of approximately 30 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.

BILLING CODE 6560-01-M

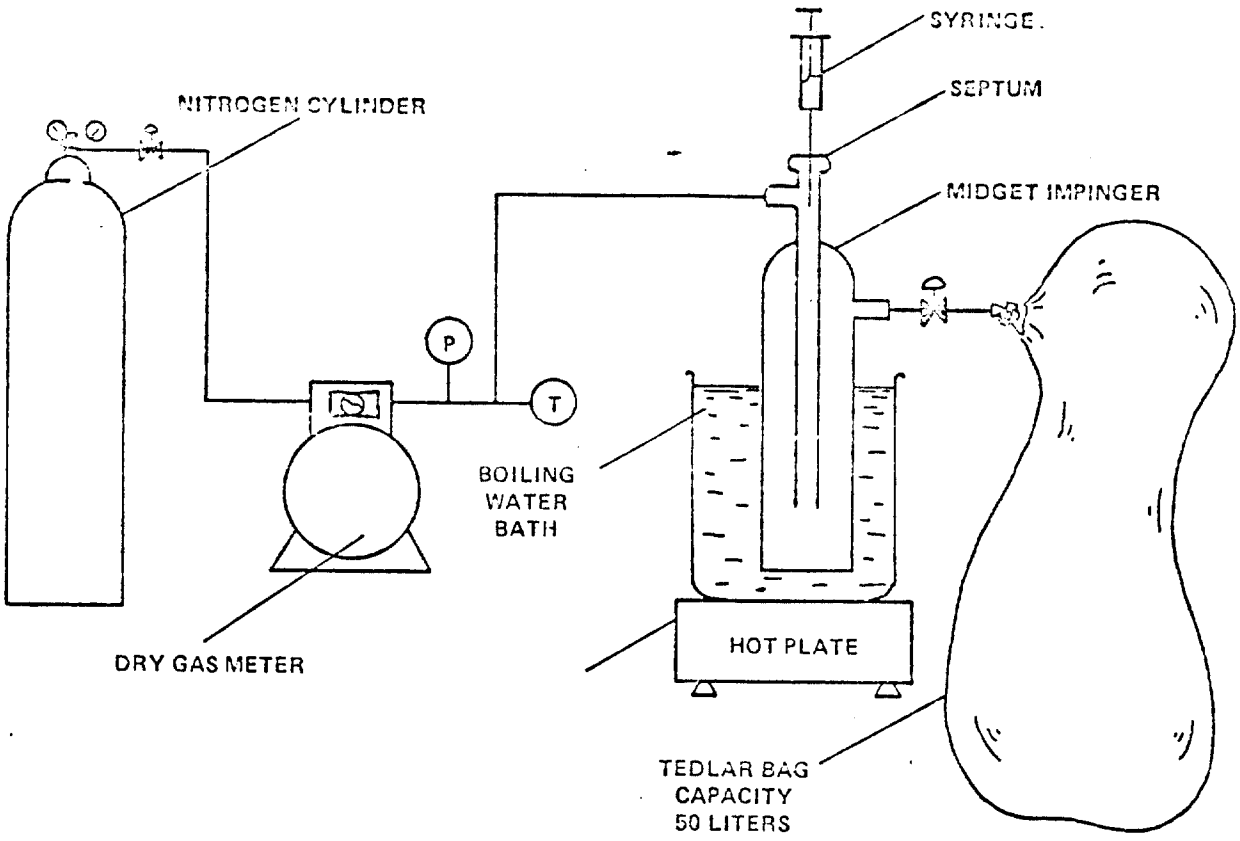


Figure 110-2. Preparation of benzene standards (optional).

BILLING CODE 6560-01-C

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, [illegible] Field Auditing [illegible].

7.3.2 Bag Leak Checks. While [illegible] is required after [illegible]. It is also advisable that it be performed before [illegible]. 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_2O (2 to 4 in. H_2O). 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_2O or 2 to 4 in. H_2O 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:

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

$$C_c = 701.9 \frac{B T_m}{V_m \; Y \; P_m} \qquad (110\text{-}1)$$

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:

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

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.

Tr = Reference temperature, the sample loop temperature recorded during calibration, °K.

S_{wb} = Water vapor content of the bag sample, volume fraction.

9. References

1. Feairheller, W. R., A. M. Kemmer, B. J. Warner, and D. Q. Douglas. Measurement of Gaseous Organic Compound Emissions by Gas Chromatography. U.S. Environmental Protection Agency. EPA Contract Number 68-02-1404. January 1978. Revised by EPA August 1978.

2. Knoll, Joseph E., Wade H. Penny, and Rodney M. Midgett. The Use of Tedlar Bags to Contain Gaseous Benzene Samples at Source Level. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Monitoring Series. EPA-600/4-78-057. October 1978.

3. Supelco, Inc. Separation of Hydrocarbons. Bellefonte, Pa. Bulletins 743A, 740C, and 74[illegible]. 19[illegible]

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 resoultion, 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 -2σ 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 $b-2\sigma_s$ to $b+2\sigma_s$, where σ_s 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.

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

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. $f_o = Q(x_1) - Q(x_2)$
8. $A_o = f_o A_c/A_s$
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.

σ_s = The standard deviation of the sample compound of interest elution curve.

σ_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.

f_o = The overlap integral.

A_o = The area overlap fraction.

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

In lieu of 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 ±10 percent, he then directs the analyst to go on the analysis of source samples. Audit supervisor judgment and/or supervisory policy determine course of action with agreement is not within ±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 of all samples. However, efforts 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 for 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.

BILLING CODE 6560-01-M

APPENDIX E

PROJECT PARTICIPANTS

APPENDIX E

PROJECT PARTICIPANTS

The following people participated in some phase of the sampling program at Bethlehem Steel, Burns Harbor, Indiana:

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

Dan Miesse, Instrument Technician

Lou Reckner, Vice President & General Manager

From Research Triangle Institute:

Peter Mehta

From U. S. Environmental Protection Agency

Lee Beck