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BENZENE SAMPLING PROGRAM AT COKE BY-PRODUCT RECOVERY PLANTS:
REPUBLIC STEEL CORPORATION
GADSDEN, ALABAMA

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

Prepared For:

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SCOTT ENVIRONMENTAL SERVICES
A Division Of
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Plumsteadville, Pennsylvania 18949

Scott Environmental Technology Inc.

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APPENDICES

1.0 INTRODUCTION

Scott Environmental Services, a division of Scott Environmental Technology, Inc. conducted a testing program at Republic Steel Corporation in Gadsden, Alabama to determine benzene emissions from one source in 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. Republic Steel 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 Republic Steel on October 16 and 17, 1980. Air and liquid samples for benzene analysis were collected from the light oil intercepting sump.

2.0 SUMMARY OF RESULTS

LIGHT OIL INTERCEPTING SUMP - TRACER DATA SUMMARY

		Benzene Emission Rate	
		lb/hr	kg/hr
Test 1	Run 1	4.27	1.94
	Run 2	4.50	2.05
Test 2	Run 1	5.41	2.46
	Run 2	5.21	2.37
Test 3	Run 1	6.29	2.86
	Run 2	5.13	2.33
	Avg.	5.14	2.38

LIQUID SAMPLE DATA

Sample Location		Date	Time	Sample Temp. (°F)	Benzene Concentration (ppm by weight)
West Side -	Inlet	10/16/80	11:25	87	25,800
	Middle	10/16/80	11:27	82	27,900
	Outlet	10/16/80	11:30	114	18.0
East Side -	Inlet	10/16/80	11:35	146	97.1
	Middle	10/16/80	11:37	139	86.7
	Outlet	10/16/80	11:40	156	1.0

3.0 RESULTS AND DISCUSSION

The light oil intercepting sump is comprised of two separate halves, called east and west for identification purposes. Figure 3-1 shows the sump configuration and location of samplers.

During sampling, the tracer gas manifold was located along the wall separating the two sides of the sump; consequently the emission rate for the entire sump was measured. The average benzene emission rate from the sump was 5.14 lb/hr.

The average benzene concentration in the organic liquid on the surface of the sumps was 27,000 ppm for the west side and 92 ppm for the east side. The concentrations in the aqueous phase which was present at the outlets were 18 and 1 ppm for the respective sides. The outlet samples were dipped from the wells at the south side of the sump, which act as skimmers or weirs by drawing the liquid at the bottom of the sump under the wall into the outlet well.

The average temperature of the liquid in the east sump was 147°F while the average temperature of the west sump was 94°F. In both sumps higher temperatures were measured at the inlets and outlets than in the middle.

The large variations in benzene concentration and temperature found across the surface of the sump suggest non-uniformity in benzene emission rates. The benzene concentration in the surface layer of the west side was 300 times that in the east side. Thus, it would be expected that most of the benzene emissions would come from the west side even though its temperature was 60°F lower than the east side. Both sumps were bottom filled, but there was some turbulence at the inlets. The turbulence

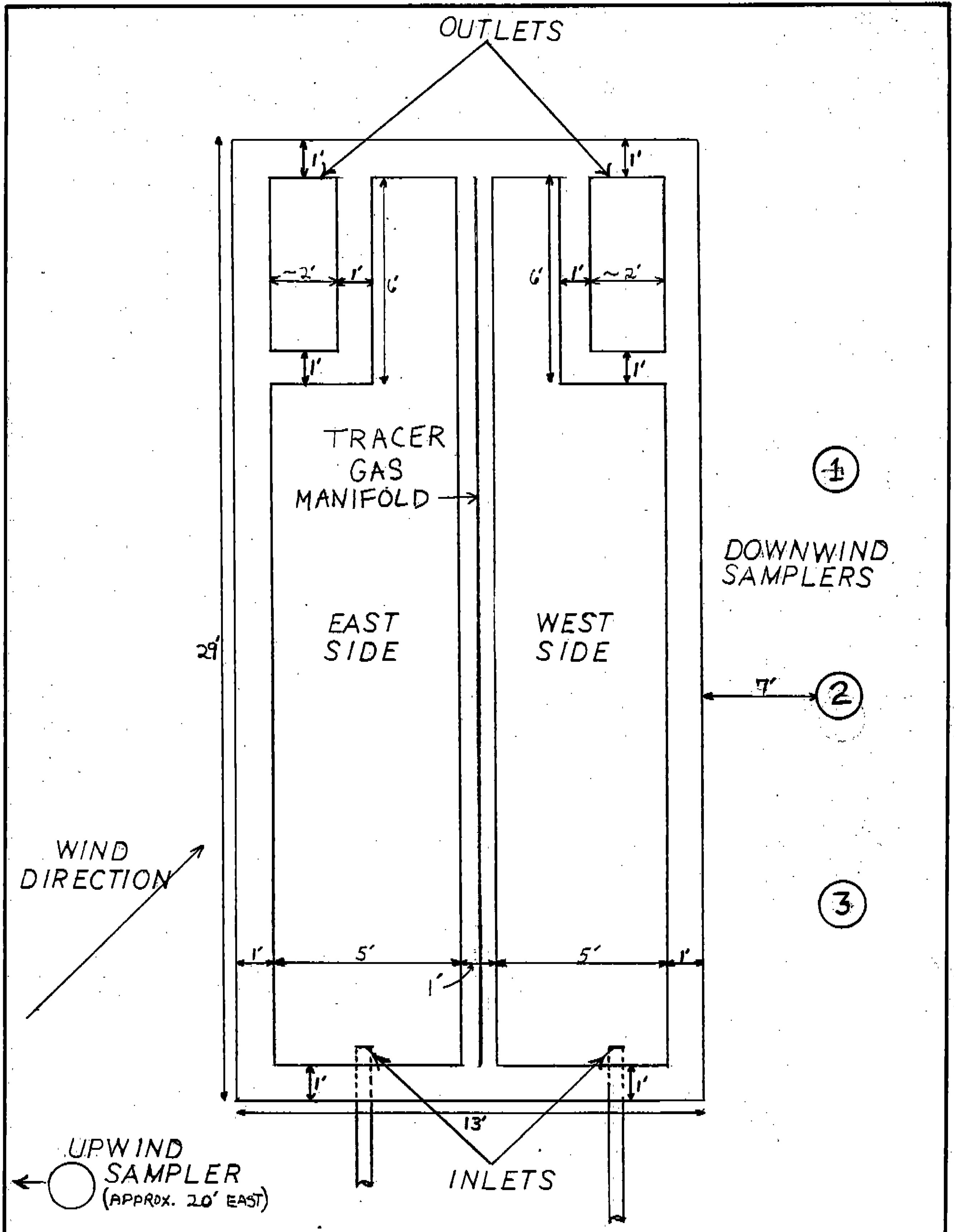

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FIGURE 3-1 LIGHT OIL INTERCEPTING SUMP

probably caused the highest emissions to occur at the inlet end of the west sump. This is believed to be responsible for the higher emission rates indicated by Sampler 3 in the first three runs (See Table 3-1). During these three runs the air flow was such that Sampler 3 was downwind of the inlet area. Overall, the run to run and sampler to sampler variations are relatively small, and there is every indication that the calculated benzene rates accurately depict the sump's emissions to the atmosphere.

TABLE 3-1

TRACER DATA

Republic Steel, Gadsden, Alabama

Sample Loc.	Conc. of Benzene (ppm)	Conc. of Isobutane (ppm)	Mass to Mass Ratio ϕ/ic_4	Benzene Emission Rate	
				(lb/hr)	(kg/hr)
10/16/80, a.m. Test #1, Run #1 Isobutane release rate: 1.16 lb/hr					
1	4.44	1.71	3.49	4.05	1.84
2	2.19	0.96	3.07	3.56	1.62
3	1.72	0.52	4.49	5.21	2.37
Upwind	0.13	N.D.			
			Avg.	4.27	1.94
10/16/80, a.m. Test #1, Run #2 Isobutane release rate: 1.16 lb/hr					
1	2.62	1.18	3.00	3.48	1.58
2	2.53	1.10	3.07	3.56	1.62
3	3.50	0.85	5.56	6.45	2.93
Upwind	0.14	N.D.			
			Avg.	4.50	2.05
10/16/80, p.m. Test #2, Run #1 Isobutane release rate: 1.15 lb/hr					
1	3.43	1.20	3.85	4.47	2.03
2	3.20	1.30	3.31	3.81	1.73
3	3.48	0.68	6.94	7.98	3.63
Upwind	N.D.	N.D.			
			Avg.	5.41	2.46
10/16/80, p.m. Test #2, Run #2 Isobutane release rate: 1.15 lb/hr					
1	4.58	1.53	4.04	4.65	2.11
2	5.25	1.40	5.05	5.81	2.64
3	3.43	1.03	4.50	5.18	2.35
Upwind	0.44	N.D.			
			Avg.	5.21	2.37

Table 3-1

(Continued)

Sample Loc.	Conc. of Benzene (ppm)	Conc. of Isobutane (ppm)	Mass to Mass Ratio ϕ/ic_4	Benzene Emission Rate (lb/hr)	Benzene Emission Rate (kg/hr)
10/17/80, a.m. Test #3, Run #1 Isobutane release rate: 1.15 lb/hr					
1	1.86	0.54	4.64	5.34	2.43
2	1.09	0.25	5.96	6.85	3.12
3	4.53	1.01	5.82	6.69	3.04
Upwind	0.61	N.D.			
			Avg.	6.29	2.86
10/17/80, a.m. Test #3, Run #2 Isobutane release rate: 1.14 lb/hr					
1	1.33	0.39	5.20	5.93	2.69
2	2.68	0.91	3.97	4.53	2.06
3	4.74	1.47	4.34	4.95	2.45
Upwind	0.61	N.D.			
			Avg.	5.13	2.60

4.0 PROCESS DESCRIPTION

The light oil intercepting sump is used to collect waste waters from the light oil refining operations. Gravity separates the oil-water waste for reclamation of the light oil. The light oil intercepting sump at Republic Steel in Gadsden, Alabama was open to the atmosphere and was 27 feet long, 11 feet wide and approximately 4 feet deep. The liquid level was approximately three feet below ground level. The sump was divided in half along its length by a wall and was actually two separate sumps, each of which had a separate inlet located on the north side of the sump and an outlet on the south side.

5.0 FIELD SAMPLING AND ANALYSIS METHODOLOGY

5.1 TRACER GAS METHOD FOR DETERMINATION OF FUGITIVE BENZENE EMISSIONS

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 benzene to the tracer gas in the sample is determined by gas chromatography. The emission rate of the 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.

5.2 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%.

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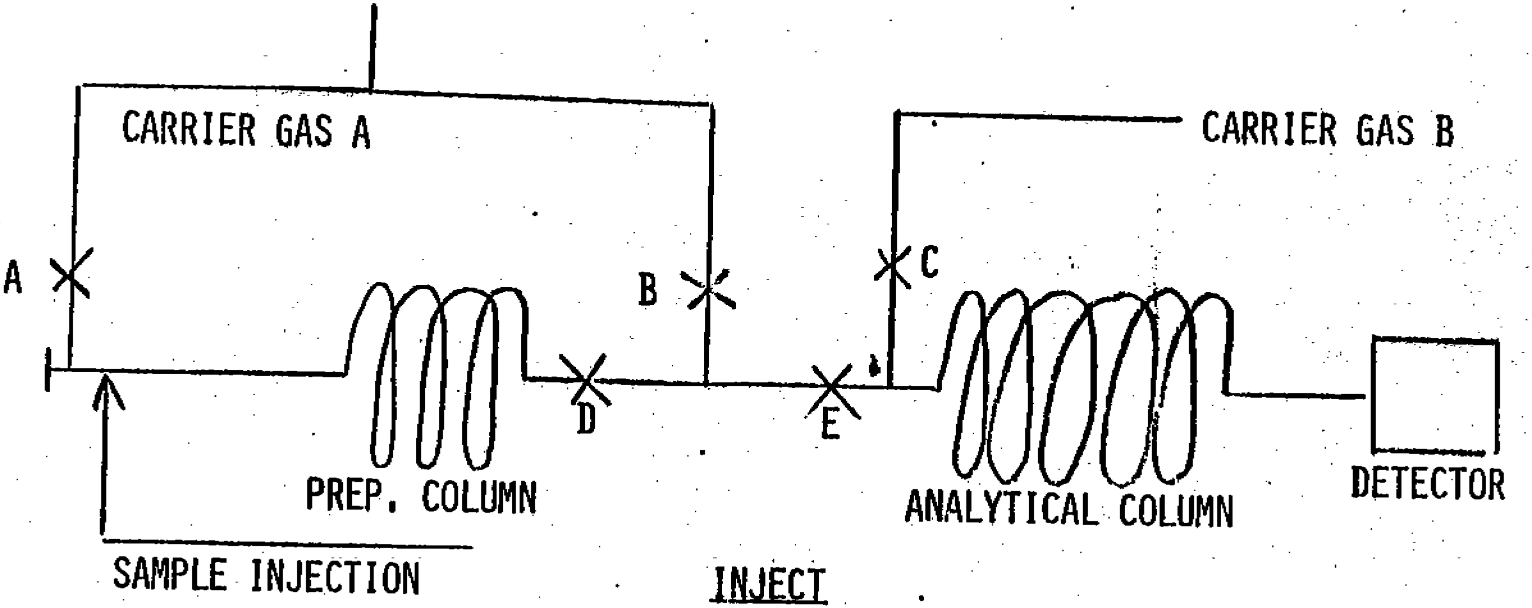
*Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.

5.3 FIELD ANALYSIS

All gas samples collected were analyzed using a Shimadzu GC Mini 1 gas chromatograph equipped with dual flame inoization detectors, dual electrometers, heated sample loop and a backflush system. Figure 5-1 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



<u>INJECT</u>

A, D, E OPEN

B, C CLOSED

<u>BACKFLUSH</u>

A, E CLOSED

B, C, D OPEN

GC COLUMN CONFIGURATION WITH BACKFLUSH

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FIGURE 5-1

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 LIGHT OIL INTERCEPTING SUMP

The sump was a fugitive emission source which was sampled using the tracer gas method. When using this method, best results are obtained by releasing the tracer gas at the liquid surface level along the central axis of the source perpendicular to the wind direction. This was accomplished for this source by placing the dispersion bar on the wall which separated the east and west sides of the sump, as depicted in Figure 3-1. The wall ran north and south and was approximately 4-6 inches above the liquid level of the sump. The tracer gas source was connected to the center of the 27 foot long dispersion bar which was comprised of six 4 1/2 foot sections joined by Swagelok connectors. On each side of the dispersion bar the holes in the bar were 19 inches apart and were of increasing size outward from the tracer source. The first section contained holes that were 0.166 inches in diameter, the second section contained holes 0.169 inches in diameter and the third section had holes that were 0.173 inches in diameter. Visual inspection of the dispersion bar at release rates typically used for testing showed that approximately the same volume of gas was exiting the holes in various sections of the bar.

Three samplers were positioned 7 feet from the sump on its west side and the presence of isobutane and benzene at the sampler locations was verified by analyzing grab samples. The upwind sampler was positioned approximately 20 feet from the sump's northeast corner.

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.

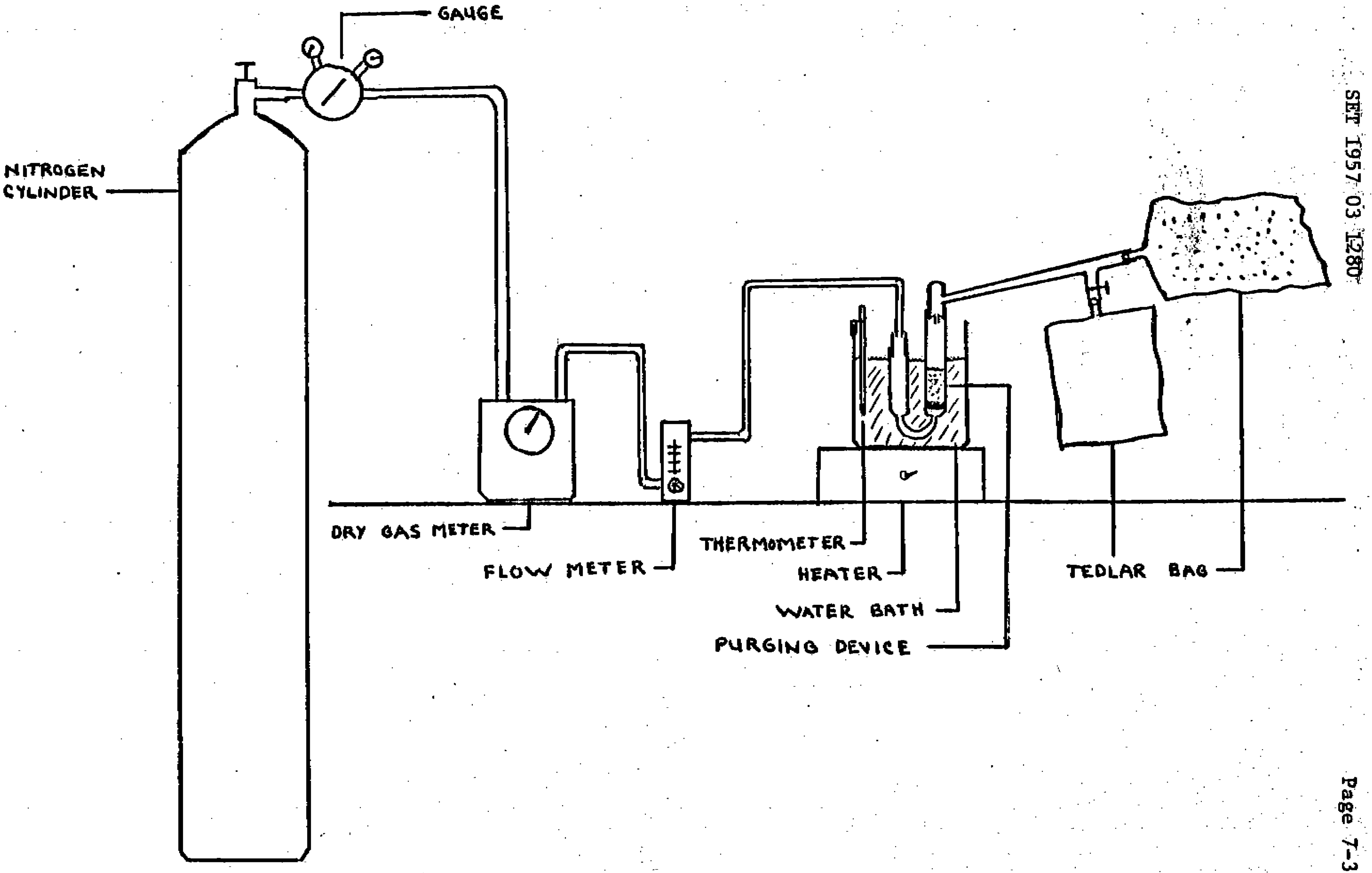


FIGURE 7-1 PURGE AND TRAP METHOD EQUIPMENT SET-UP

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 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 ±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

Example: Test 1, Run 1, Sampler 1

Concentration of benzene:	4.44 ppm
Concentration of isobutane:	1.71 ppm
Isobutane release rate:	1.16 lb/hr.

Calculation of Mass to Mass Ratios:

Benzene 4.44 ppm X 78 g/mole = 346.32

Isobutane 1.71 ppm X 58 g/mole = 99.18

$$\frac{346.32}{99.18} \text{ X } 1.16 \text{ lb/hr.} = 4.05 \text{ lb/hr. benzene}$$

APPENDIX B

FIELD DATA SHEETS

TEST 1

RUNS 1 & 2

SCOTT ENVIRONMENTAL TECHNOLOGY, INC.

PROJECT 1922

TRACER GAS DATA SHEET

Page B-1

PLANT: Republic, Gadsden

PROCESS: Sump

PROCESS NOTES:

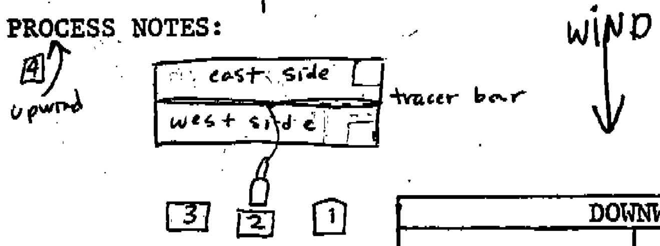
DATE: 10/16/80

WIND SPEED: light

WIND DIRECTION: east

AMBIENT TEMPERATURE:

BAROMETRIC PRESSURE:



	DOWNWIND						UPWIND	
Sampler Number	1		2		3		4	
Distance from Source	7 ft		7 ft		7 ft		20 ft	
Sampling Rate	10 lph		10 lph		10 lph		10 lph	
Pump Numbers	5		10		8			
Tedlar bag numbers	1	5	2	6	4	7	~~4~~3	8
Start Time	8:30	9:05	8:30	9:05	8:30	9:05	8:35	9:05
Stop Time	9:00		9:00		9:00		9:00	

Gas meter Y = 1.059

ISOBUTANE RELEASE: Gas Temperature

TIME	METERED VOLUME	
8:30 0	244.050	
2	244.302	
4	244.550	
6	244.795	
8	245.038	
10	245.281	.123
13	245.642	
14	245.763	
16	246.030	
18	246.240	
20	246.472	.119
22	246.704	
24	246.943	
26	247.194	
28	247.442	
30	247.692	.122

Gas Pressure

TIME	METERED VOLUME	
9:05 0	248.325	
2	248.578	
4	248.832	
6	249.082	
8	249.332	
10	249.579	.125
12	249.827	
14	250.074	
16	250.315	
18	250.555	
20	250.887	.131
22	251.025	
24	251.261	
26	251.492	
28	251.720	
30	251.951	

Sampers about 4 feet apart, 7 ft. from railing of sump.

3.642 ft³/30 min = .1214 cfm
× 1.059
0.1286 cfm

3.626 ft³/30 min = 0.1209 cfm
× 1.059
0.1280 cfm

TEST 2
RUNS 1 & 2

SCOTT ENVIRONMENTAL TECHNOLOGY, INC.

TRACER GAS DATA SHEET

PROJECT 1922 (4 upwind)

PLANT: Republic - Gadsden Ala

PROCESS: Sump

PROCESS NOTES:

DATE: 10/16/80

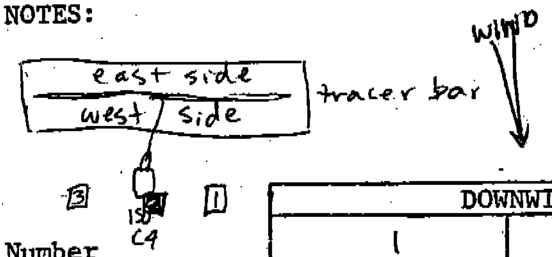
WIND SPEED: light

WIND DIRECTION: east

AMBIENT TEMPERATURE:

BAROMETRIC PRESSURE:

liquid ~4 ft deep. West side has ~1 ft sludge on bottom



	DOWNWIND						UPWIND	
Sampler Number	1		2		3		4	
Distance from Source	7 ft		7 ft		7 ft		~ 20 ft.	
Sampling Rate	10 lph		10 lph		10 lph		10 lph	
Pump Numbers								
Tedlar bag numbers	9	13	10	14	11	15	12	3
Start Time	9:40	11:02	9:40	11:02	9:40	11:02	9:40	11:02
Stop Time								

Gas meter Y = 1.059

ISOBUTANE RELEASE: Gas Temperature

TIME		METERED VOLUME	
9:40	0	252.460	
	2	252.686	
	4	252.935	
	6	253.182	
	8	253.429	
	10	253.672	.121
	12	253.917	
	14	254.158	
	16	254.400	
	18	254.640	
	20	254.877	.1205
	22	255.109	
	24	255.338	
	26	255.573	
	28	255.822	
	30	256.072	

Gas Pressure

TIME		METERED VOLUME	
11:02	0	260.210	
	2	260.451	
	4	260.702	
	6	260.949	
	8	261.197	
	10	261.437	.1227
	12	261.670	
	14	261.899	
	16	262.132	
	18	262.361	
	20	262.590	.116
	22	262.832	
	24	263.086	
	26	~~263.3[illegible]7~~	
	28	263.581	
	30	263.830	

3.612 ft³/30 min = .1204 cfm
x 1.059 = .1275 cfm

~~[illegible]~~

3.620 ft³/30 min = .1206 cfm
x 1.059
0.1277 cfm

TEST 3
RUNS 1 & 2

SCOTT ENVIRONMENTAL TECHNOLOGY, INC.

PROJECT 1922

TRACER GAS DATA SHEET

PLANT: Republic - Gadsden, Alabama
PROCESS: Lt. oil sump
PROCESS NOTES:
inlet end on east side is bubbling
west side very sludgy

DATE: 10/16/80
WIND SPEED: light
WIND DIRECTION: east
AMBIENT TEMPERATURE:
BAROMETRIC PRESSURE:

	DOWNWIND						UPWIND	
Sampler Number	1		2		3		4	
Distance from Source	7 ft		7 ft		7 ft		~ 20 ft	
Sampling Rate	10 lph		10 lph		10 lph		10 lph	
Pump Numbers								
Tedlar bag numbers	1/3	1	1/2	2	3/4	4	8	
Start Time	1:30	2:05	1:30	2:05	1:30	2:05	1:30	
Stop Time	2:00	2:35	2:00	2:35	2:00	2:35	2:35	

Gas meter Y = 1.059

ISOBUTANE RELEASE: Gas Temperature

TIME		METERED VOLUME	
1:30	0	264.510	
	2	264.758	
	4	264.998	
	6	265.230	
	8	265.456	
	10	265.689	.118
	12	265.932	
	14	266.175	
	16	266.424	
	18	266.664	
	20	266.900	.119
	22	267.144	
	24	267.395	
	26	267.642	
	28	267.888	
	30	268.131	

Gas Pressure

TIME		METERED VOLUME	
2:05	0	268.800	
	2	269.045	
	4	269.299	
	6	269.545	
	8	269.788	
	10	270.026	.1226
	12	270.262	
	14	270.497	
	16	270.722	
	18	270.949	
	20	271.162	.114
	22	271.404	
	24	271.657	
	26	271.902	
	28	272.148	
	30	272.389	

3.621 ft³/30 min = .1207 cfm
x 1.059
0.1278 cfm

3.589 ft³/30 min = .1196 cfm
x 1.059
0.1267 cfm

PROJECT 1906 BENZENE/BaP PRESURVEY

SAMPLE DATA

Plant Republic-Gadsden Ala Process Sump Date 10/16/80

Sample No. west side inlet Time Sampled

Sample Type: [✓ Liquid] Air

Sample Temperature 87°F

Ambient Temperature

Description of Sampling Location:

Sample No. west side middle Time Sampled

Sample Type: [✓ Liquid] Air

Sample Temperature 82°F

Ambient Temperature

Description of Sampling Location:

Sample No. west side outlet Time Sampled

Sample Type: [✓ Liquid] Air

Sample Temperature 114°F

Ambient Temperature

Description of Sampling Location:

SAMPLE DATA

Plant Republic-Gadsden Ala Process Sump Date 10/16/80

Sample No. East side inlet Time Sampled 11:35

Sample Type: [✓ Liquid] Air

Sample Temperature 146 °F

Ambient Temperature

Description of Sampling Location:

Sample No. east side middle Time Sampled 11:37

Sample Type: [✓ Liquid] Air

Sample Temperature 139 °F

Ambient Temperature

Description of Sampling Location:

Sample No. east side outlet Time Sampled 11:40

Sample Type: [✓ Liquid] Air

Sample Temperature 156 °F

Ambient Temperature

Description of Sampling Location:

Scott Environmental Technology Inc.

APPENDIX C

LABORATORY DATA SHEETS

CHROMATOGRAPHIC ANALYSIS LOG

Republic Steel, Gadsden Ala

Project No. 1957 Date 9/6/80 Analyst TB

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
9:00	Std 6.11 ppm φ	59.75	0.102		
	1000 ppm iC4	11.0	0.096		
	64×10^4 - 1 Range				
					Average ~~[illegible]~~
	Test #1 Run #1 Bag #1		.048	~~[illegible]~~ 1.74	
	Iso C4 - 32×10^4	35.5	~~0.048~~ ~~[illegible]~~	~~[illegible]~~ ×55 =	99.18 > 3.49 (5)
	φ - 64×10^4	43.5	0.102	4.44×78 =	346.32
	Test #1 Run #1 Bag #2				
	Iso C4 - 64×10^4	10	0.96	0.96 × 58 =	55.68 > 3.07 (17)
	φ - 64×10^4	21.5	~~[illegible]~~ 0.102	2.19×78 =	170.82
	Test #1 Run #1 Bag #4				
	Iso C4 - ~~32~~ 16×10^4	21.5	0.026	0.52×58	29.93 > 1.49 (15)
	φ - ~~64~~ 16×10^4	69	0.026	1.72×78	134.55
	Test #1 Run #1 Bag #3				
	Manual φ - 16x	5	.026	0.13 15	
	iC4 - 16x	<10			

CHROMATOGRAPHIC ANALYSIS LOG

Republic Steel Gadsden Ala.

Project No. 1957 Date 10/[illegible]/80 Analyst TB

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	Truscon Steel				
	64 ppm C_4 - 64x10⁴	62.5	0.099		Average = 3.88
	106 ppm iC_4 - 32x10⁴	22.5	.047		
	Test #1 Run #2 Bag #5				
	Iso-C_4 - 64x10⁴	26	~~0.050~~ 0.099	1.18 ~~2.62~~ x 58	6815 > 3.00
	ϕ - 64x10⁴	12.5	~~0.047~~ 0.094	~~1.18~~ 2.62 x 78	204.36
	Test #1 Run #2 Bag #6	~~50.5~~			
	Iso-C_4 - 32x10⁴	50.5	0.050	~~2.53~~ 1.10 x 58	6406 > 3.07
	ϕ - 32x10⁴	23.5	0.047	~~1.10~~ 2.53 x 78	196.95
	Test #1 Run #2 Bag #7				
	Iso-C_4 - 32x10⁴	70	0.050	0.85 x 58	4907 > 5.56
	ϕ - 32x10⁴	18	0.047	3.50 x 78	273.0
	Test #1 Run #2 Bag #8				A
	Iso-C_4 - 8x10⁴	ND			
	ϕ - 8x10⁴	11	0.013	0.14 ppm	

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CHROMATOGRAPHIC ANALYSIS LOG

[illegible] Pla.

Project No, 1957 Date 9/10/80 Analyst TB

Time	Sample Identification	Peak 1 Height/Area	Concentration Factor	Concentration	Comments
	Bag Blank. Bag 1/2 8 x 10⁴	9 - ϕ	.012	.108	
	Bag 3/4 8 x 10⁴	7 - ϕ	.012	.084	
	Bag 1/3 8 x 10⁴	5 - ϕ	.012	.06	
	Bag #1	ϕ - 3	.012	.036	
		K4 - 10	.011	.11	
	Bag #2	ϕ - 2	.012	.024	
		K4 8	.011	.088	
	Bag #4	ϕ - 10	.012	.12	
		K4 - 12	.011	.132	

CHROMATOGRAPHIC ANALYSIS LOG

Republic Steel, Gadsden Ala.

Project No. 1957 **Date** 10/2/80 **Analyst** TB

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	Frozen Std				
	iC4 - 32×10^4 - 1.06ppm	21	.050		Average = 4.70
	ϕ - 64×10^4 - 6.11ppm	59	.104		
	Test #2 Run #1, Bag #9				
	iC4 - 64×10^4	12	.100	1.2×58 =	696 > 3.85
	ϕ - 64×10^4	33	.104	343×78 =	26230
	Test #2 Run #2 Bag #10				
	iC4 - 32×10^4	26	.050	1.3×58 =	75.4 > 3.31
	ϕ - 32×10^4	61.5	.052	320×78 =	249.44
	Test #2 Run #1, Bag #11				
	iC4 - 32×10^4	13.5	.050	0.68×58 =	39.15 > 6.94
	ϕ - 32×10^4	67	.052	348×78 =	271.75
	Test #2 Run #1 Bag #12				
	iC4 16×	×10.			
	ϕ 16×	.3			

CHROMATOGRAPHIC ANALYSIS LOG

Republic Steel, Gadsden Ala.

Project No. 1457   Date 10/10/80   Analyst TB

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	Trace Std				
	6.11 ppm ø - 64×10^4	59.5			Average 4.53
	1.06 ppm iC4 - 32×10^4	21			
	Test #2 Run #2 Bag #14				
	iC4 32×10^4	30.5	.05	1.53×58 =	88.45 > 4.04
	ø - 64×10^4	44	.104	4.58×78	356.93
	Test #2 Run #2 Bag #13				
	iC4 64×10^4	14	.10	1.4×58	81.2 > 5.05
	ø 64×10^4	50.5	.104	5.25×78	409.66
	Test #2 Run #2 Bag #15				
	iC4 32×10^4	20.5	0.05	1.03×58 =	59.45 > 4.50
	ø 64×10^4	33	0.104	3.43×78 =	267.70
	Std				
	6.11 ppm ø - 64×10^4	62			
	1.06 ppm iC4 - 32×10^4	22			
	Test 2 Run 2 Bag #3				
	Upwind 16×10^4				
	iC4	ND	.026		
	~~ø~~	17		.44	

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CHROMATOGRAPHIC ANALYSIS LOG

Republic Steel, Gadsden, Ala

Project No. 1957 Date 10/17/80 Analyst TB

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	Inner Std. Cell 115ppm ϕ - 64×10^4 1060ppm nC_4 - 32×10^4	58 215	0.105 0.049		Average - 5.47
	Test #3 Run #1 Bag #1/2 nC_4 ~~ϕ~~ - 32×10^4 ϕ ~~nC_4~~ - 32×10^4	11 35.5	.049 .053	0.54 x 58 = 1.86 x 78 =	3132 145.37 > 4.64
	Test #3 Run #1 Bag #1/3 ϕ - 32×10^4 nC_4 - 32×10^4	20.5 5	.053 .049	1.09 x 78 = 0.25 x 58 =	84.78 1421 > 5.96
	Test #3 Run #1 Bag #1/4 ϕ - 32×10^4 nC_4 - 32×10^4	82 20.5	.053 .049	4.63 x 78 = 1.01 x 58 =	338.98 58.26 > 5.82
	Repeat Bag #1 Stability ϕ 32×10^4 nC_4 32×10^4	55 12	.053 .049	2.92 x 78 = 0.58 x 58 =	227.37 3416 > 666

Scott Environmental Technology Inc

Scott Environmental Technology Inc.

CHROMATOGRAPHIC ANALYSIS LOG

[illegible] Std, [illegible]

Project No. 1957 Date 10/17/80 Analyst TS

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	Test #3 Run #2 Bag #1				
	C4 - 32x10^4	7	.049	0.34 x 58 =	19.89 > 5.20
	Ø - ~~64~~ 32 x10^4	25	~~0~~ .053	1.33 x 78 =	103.35
	Trace Std				
	6.11 ppm Ø - 64x10^4	58			
	1.06 ppm C4 - 32x10^4	21			
	Test #3 Run #2 Bag #2				
	C4 - 32x10^4	18.5	.049	0.91 x 58 =	52.55 > 3.97
	Ø - 32x10^4	50.5	.053	2.68 x 78 =	208.77
	Test #3 Run #2 Bag #4				
	C4 - 32x10^4	30	.049	1.47 x 58 =	85.20 > 4.34
	Ø - 32x10^4	89.5	.053	4.74 x 78	369.99
	Repeat Bag #6 - Stability				
	C4 - 32x10^4	23.5	.049	1.15 x 58 =	66.70 > 3.13
	Ø - 32x10^4	50.5	.053	2.68 x 78 =	209.09
	Repeat Bag #13 Stability				
	C4 - 64x10^4	14	.098	1.37 x 58 =	79.58
	Ø 64x10^4				

CHROMATOGRAPHIC ANALYSIS LOG

Project No.__________ Date__________ Analyst__________

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	Tracer Std				
	6.11 ppm φ - 61 x 10^4	61			
	1.06 ppm ACy - 32 x 10^4	23			
	Test #3 Run #12 Bag #8				
	ACy - 8 x 10^4	10			
	φ - 8 x 10^4	46	0.013	0.61	
	Std 122.5 ppm φ				
	128 x 10^3. 100 Dno.				
	Grab @ Samp Inlet				
	128 x 10^3 -				
	Grab @ Samp Middle				
	Jon Side				

APPENDIX D

TRACER GAS METHOD DEVELOPMENT

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.

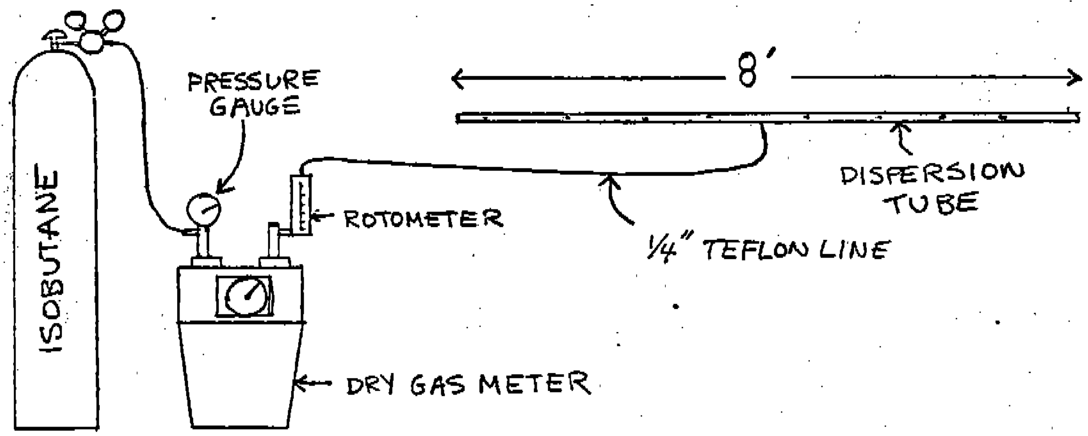
For the determination of benzene emissions at secondary by-products plants, isobutane is the recommended tracer gas. The second choice for a tracer gas is a halogenated hydrocarbon. At secondary by-products plants the hydrocarbons in the background atmosphere are almost exclusively emissions from the 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.

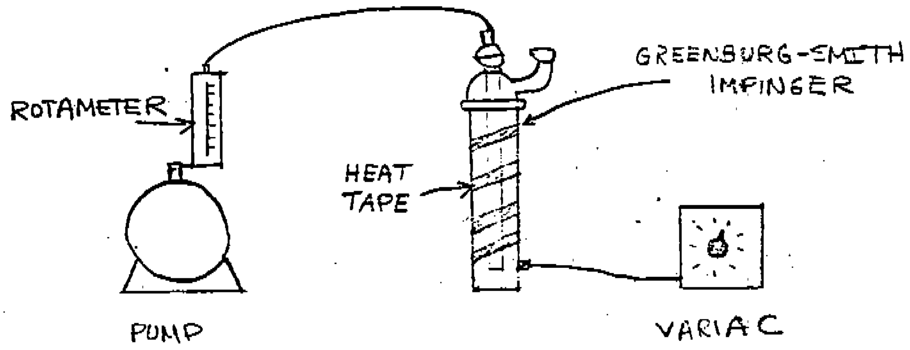
Two different dispersion tube configurations were tested, both were constructed from 1/4" O.D. stainless steel tubing. The first tube tested was 8' long with the tracer source connected to one end of the tube. The tube contained holes every 19" which were progressively larger moving away from the gas 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.

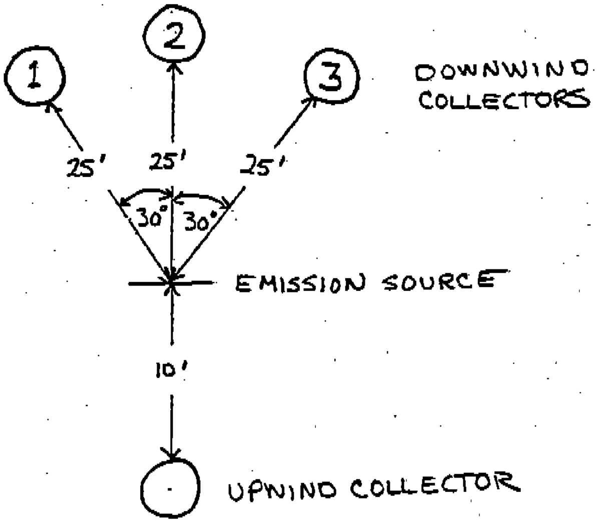
Benzene was also released in two ways; by evaporation and a heated bubbler. Both methods proved adequate for experimental determinations. When evaporation was used to release benzene, a stainless steel pan 16" x 24" x 1/2" was employed to contain the benzene. During an experimental determination benzene 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^{o} 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 quantative 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 condusive 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 conditons 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° 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 $T\phi/ic_4$	ϕ/ic_4 #1	ϕ/ic_4 #2	ϕ/ic_4 #3	Average
ϕ 0.027 ic_4 5.26	Evaporation	Grab	0-5 MPH	Steady	0.005	*NO	NO	NO	---
ϕ 0.993 ic_4 8.27	Evaporation	Grab	0-5 MPH	Steady	0.120	*NO	NO	NO	---
ϕ 4.05 ic_4 7.16	Evaporation	Grab	0-5 MPH	Steady	0.59	0.64	0.64	0.65	0.645
ϕ 9.40 ic_4 6.38	Evaporation	Integrated	5-10 MPH	Steady	1.47	1.57	1.43	---	1.50
ϕ 10.85 ic_4 13.59	Evaporation	Integrated	20-25 MPH	Variable	0.80	1.29	1.82	0.94	1.35
ϕ 9.40 ic_4 8.25	Bubbler	Integrated	15-20 MPH	Steady	1.14	1.40	1.93	1.02	1.18
ϕ 6.33 ic_4 6.48	Bubbler	Integrated	0-5 MPH	Steady	0.91	0.97	0.96	0.96	0.96
ϕ 6.48 ic_4 6.48	Bubbler	Integrated	0-5 MPH	Steady	1.00	0.91	0.86	0.89	0.89

ϕ - Benzene

ic_4 - Isobutane

* No benzene, only isobutane detected.

APPENDIX E

PROJECT PARTICIPANTS

E

APPENDIX E

PROJECT PARTICIPANTS

The following people participated in some phase of the sampling program at Republic Steel, Gadsden, Alabama.

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 & General Manager

From Research Triangle Institute:

- Peter Mehta

From U. S. Environmental Protection Agency

- Dan Bivins

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: Republic Steel Corporation

Location: Gadsden, Alabama

Project Report Number: 80-BYC-4

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 IV
(copy enclosed for State agency)
Bob Kilgore, EPA Library Services (MD-35)