Note: This is a reference cited in *AP 42, Compilation of Air Pollutant Emission Factors, Volume I Stationary Point and Area Sources.* AP42 is located on the EPA web site at www.epa.gov/ttn/chief/ap42/

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HEADSPACE BENZENE CONCENTRATION OVER LIQUID SAMPLES FROM COKE BY-PRODUCT PLANTS

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Work Assignment 3

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1.0 INTRODUCTION

Scott Environmental Services conducted a benzene sampling program at seven coke by-product plants during the summer of 1980 for the U.S. Environmental Protection Agency. Fugitive process emissions from sources were determined by measuring the benzene concentration in the stack gas and the gas flow rate and temperature. Process liquid samples were also collected from each source.

A test program was conducted to determine if any correlation existed between the benzene emission rate from a process and the benzene concentration in the headspace over a liquid sample from that process. If a correlation existed it would allow emission rate estimates based on a simple laboratory procedure rather than on field sampling procedures.

Laboratory tests were performed on liquid samples from eight confined sources. The samples were heated in enclosed vessels and headspace samples were extracted and analyzed by gas chromatography. Two separate sets of experimental conditions were used. Initially the samples were heated to process temperature in vented flasks. Due to the great variability in the results a new procedure was devised wherein the samples were all heated to 212°F while maintaining a constant pressure as thermal expansion of the headspace gas occurred. No gas was vented.

The following sections present the results and analytical procedures of the vapor headspace sampling program.

2.0 RESULTS

Table 2-1 presents the results of the headspace sampling at 212°F (unvented) and the calculated ratios of headspace/liquid concentrations, headspace/stack gas concentrations, and stack gas/liquid concentrations. The results of the headspace sampling at process temperatures (vented) are shown in Table 2-2, with the ratios of headspace at 212°F/headspace at process temperature and headspace at process temperature/stack concentration. The two tar decanters are not included in Table 2-2 because the headspace benzene concentrations were not measured at process temperature.

All the process samples used in this program were dipped from the liquid surface through a hatchway, with the single exception of the tar dehydrator at Burns Harbor, where the sample was collected from a pump at the tank outlet.

TABLE 2-1 HEADSPACE BENZENE CONCENTRATIONS AT 212°F

Source/Plant	Sample Composition	Process Temp. t (°F)	(S) Stack Benzene Conc. (ppm-V)	(L) Liquid Benzene Conc. (ppm-Wt)	(H) Headspace Benzene Conc. At 212°F (ppm-V)	H/L Ratio	H/S Ratio	S/L Ratio
Wash Oil Decanter (F)	Oil	205	817	44	1404	32	1.7	18.6
Tar Decanter (BH)	Aqueous	120	2473	92	2388	26	1.0	26.9
Tar Decanter (B)	Aqueous	178	1380	5	336	64	0.3	230
Tar Dehydrator-W (F)	Heavy Tar	207	1757	621	4261	6.9	2.4	2.9
Tar Dehydrator-E (F)	Heavy Tar	219	2080	276	1390	5.5	0.7	7.4
Tar Dehydrator (BH)	Whole Tar	162	9133	1987	12385	6.3	1.4	4.7
Tar Storage (P)	Aqueous	145	630	33	2550	70.0	3.7	19.1
Tar Storage (M)	Aqueous	168	1825	N.A.	1402	--	0.8	--

(F) = Fairless
(BH) = Burns Harbor
(B) = Bethlehem
(P) = Pueblo
(M) = Monessen

TABLE 2-2 HEADSPACE BENZENE CONCENTRATIONS AT PROCESS TEMPERATURES

Source/Plant	Process Temp. t (°F)	H_t Headspace* Benzene Conc. at t (ppm-V) Avg.	Max.	H Headspace** Benzene Conc. at 212°F (ppm-V)	H/H_t Ratio	H_t/Stack Ratio
Wash Oil Decanter (F)	205	179	189	1404	7.8	0.22
Tar Dehydrator-W (F)	207	1273	1273	4261	3.3	0.72
Tar Dehydrator-E (F)	219	521	521	1557	3.0	0.25
Tar Dehydrator (BH)	162	2346	5296	12385	5.3	0.26
Tar Storage (P)	160	75	193	2309	30.8	0.12
Tar Storage (M)	169	252	622	1402	5.6	0.14

*Vented headspace procedure

**Confined headspace procedure

3.0 DISCUSSION OF RESULTS

The lack of any close correlation between the headspace benzene concentration and the source concentration measured in the field tests of multi-phase processes is due to the many other variables which affect the benzene emitted by these sources. These variables include:

1. Type of Process - continuous, steady state; continuous, variable; batch.
2. Nature of Material - tar, oil, aqueous, combination of tar and aqueous.
3. Dynamic residence time of continuous processes.
4. Degree of agitation of process material.
5. Concentration of water and light organics in tars and oils.
6. Thickness of aqueous layer in aqueous organic systems.
7. Process headspace volume vs. process surface area.
8. Temporal variations in temperature, liquid level, liquid composition, throughput, etc.
9. Ambient temperature and pressure.

The liquid samples chosen for this test program were those collected from confined sources, i.e. covered and vented to the atmosphere, because the conditions affecting open sources would introduce many more variables into the data analysis.

Each of the above factors has an impact on the concentration and rate of benzene emissions. A detailed discussion of the role of each variable is beyond the scope of this task, but a brief discussion of a tar decanter will demonstrate the complex nature of these systems. Tar decanters are used to separate mixtures of tar and ammonia liquor from primary coolers and battery collector mains into liquor, tar and sludge. The tar decanter tested at Bethlehem Steel, Bethlehem, Pennsylvania yielded benzene concentrations of 720 to 1980 ppm in the vent during three test runs. The flushing liquor sampled from the surface (180°F) which contained 5 ppm (wt) benzene gave a headspace benzene concentration of 386 ppm at 212°F. The incoming material from the primary cooler contained approximately 20% tar and 80% flushing liquor. The flushing liquor contained 16 ppm (wt) benzene and the tar 1800 ppm (wt). Headspace gas from this material contained 41,000 ppm benzene which

is 100 times the concentration in the corresponding surface liquor (no tar) analysis. This demonstrates the transfer of benzene from the tar to the flushing liquor and then to the headspace in the laboratory analysis. In the actual process, the tar decanter contains a tar layer beneath the surface flushing liquor yet the measured benzene concentration was 20 to 50 times less than in the laboratory test of the tar/liquor sample. In fact, the measured process concentrations average only 2 to 5 times the laboratory result from the liquor alone. The most likely factor limiting the actual process emission is the thickness (depth) of the liquor layer. The thickness of the liquor layer was not measured but can be assumed to be at least 1 to 2 feet. In the laboratory test, the liquor layer in the flask was less than one inch thick, thus facilitating transfer of the benzene in the tar to the headspace. If the tar decanter were operated as a static (batch) process, it would be expected that the benzene concentration would approach the 41,000 ppm value obtained in the lab test. However, during normal operations as a continuous flow system with a short dynamic residence time, the benzene concentration remained less than 2,000 ppm.

The above data demonstrate that the benzene emissions from a complex multi-phase system cannot be estimated from simple laboratory tests. The relatively few confined, multi-phase systems included in the field test program and the limited information available on process variables preclude any further search for a means of estimating emissions from such sources.

Further work would have to be based on more extensive field data and on complex phase transfer and boundary layer theory and experiment.

4.0 ANALYTICAL PROCEDURES

Two separate sets of experimental conditions were used to measure headspace benzene from samples collected from confined sources. Initially headspace benzene concentrations were measured with the liquid sample at process temperature in a vented flask. Experimental procedures were subsequently revised such that headspace benzene was measured with the liquid sample at 212°F without any venting. 212°F was chosen because it provided a convenient way to maintain a stable sample bath temperature.

For the first series of determinations at process temperature, 25 cc of the liquid sample was placed in a graduated glass vessel which was fitted with a ground glass joint. The vessel top had a single port which was covered by a small rubber septum. A 20 gauge syringe needle was inserted in the septum for the purpose of relieving pressure and simulating the process vent. The samples were heated by immersing the vessel in a beaker of water which was maintained at the process temperature. Samples were allowed to equilibrate in the water bath for approximately 15 minutes prior to extraction of headspace gas samples for injection into the chromatograph.

From the triplicate liquid samples collected from each process, an aliquot of a single sample was anlyzed for the tarry materials and a composite of all three samples was analyzed for the less viscous liquids. Replicated determinations were not done during this phase of the analysis. Chromatographic data for consecutive injections of the same sample show a significant degree of variability.

This lack of replicability was attributed to problems in maintaining a constant bath temperature and also to the open vent in the top of the vessel, which was releasing benzene from the vessel and consequently changing the concentration of benzene in the headspace. The experimental procedure was revised such that all samples were heated to 212°F in a boiling water bath, and a 20 cc or 50 cc syringe was used in place of the open syringe needle, to relieve pressure without releasing benzene as the sample was heated. This created a more stable equilibrium in the sample vessel prior to extraction of a headspace sample for analysis. Chromatographic data for this second procedure had a higher degree of precision than did the previous analysis.

For the chromatographic analysis of most samples it was necessary to dilute samples before injection into the chromatograph. Dilutions were typically by a factor of 10 or 20.

All gas samples 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.

The samples were drawn into a glass syringe and 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 laboratory 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

APPENDIX A

FIELD DATA SHEETS

LIQUID SAMPLES

PROJECT 1906 BENZENE/BaP PRESURVEY

SAMPLE DATA

Plant Bethlehem St. Bethlehem Process Tar decanter #5 battery Date 7/8/80

Sample No. TD 1 Time Sampled 15:25

Sample Type: (Liquid) Air

Liquid ~ 2ft below top of decanter

Sample Temperature 80°C

Ambient Temperature

Description of Sampling Location: Dipped from hatchway on top of tar decanter at outlet end

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Sample No. TD 2 Time Sampled 16:00

Sample Type: (Liquid) Air

Skimmed from surface

Sample Temperature 82°C

Ambient Temperature

flushing liquor

Description of Sampling Location: dipped from hatchway at outlet end of decanter

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Sample No. Time Sampled

Sample Type: Liquid Air

Sample Temperature

Ambient Temperature

Description of Sampling Location:

PROJECT 1906 BENZENE/BaP PRESURVEY

SAMPLE DATA

Plant Beth. Steel, Bethlehem Process Tar decanter, #5 battery Date 7/9/86

Sample No. TD 5 Time Sampled 15:45

Sample Type: (Liquid) Air

Sample Temperature 140 °C °F

Ambient Temperature ~95 °F

Description of Sampling Location:

Flushing liquor outlet from primary coolers

Sample No. TD 6 Time Sampled 15:45

Sample Type: (Liquid) Air

Sample Temperature 140 °C °F

Ambient Temperature ~95 °F

Description of Sampling Location:

same

Sample No. Time Sampled

Sample Type: Liquid Air

Sample Temperature

Ambient Temperature

Description of Sampling Location:

PROJECT 1957 07 0181

SAMPLE DATA

Plant Buens 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 3 outlet

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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.

PROJECT 1906 BENZENE/BaP PRESURVEY

SAMPLE DATA

Plant _____ Process _____ Date _____

Sample No. _____ Time Sampled _____

Sample Type: Liquid Air

Sample Temperature _____

Ambient Temperature _____

Description of Sampling Location:

Sample No. _____ Time Sampled _____

Sample Type: Liquid Air

Sample Temperature _____

Ambient Temperature _____

Description of Sampling Location:

Sample No. Tar Storage 1,2,3 Time Sampled 5:00 pm

Sample Type: Liquid Air

Sample Temperature 145 °F

Ambient Temperature _____

Description of Sampling Location:

SAMPLE DATA

Plant US Steel Fairless Process Tar dehydrator Date 9/1/80

Sample No. Inlet to 1st tank (1,2,3) Time Sampled 6:05

Sample Type: (Liquid) Air

Sample Temperature 196 °F

Ambient Temperature

Description of Sampling Location: from funnel feeding 1st tar dehydr.

Sample No. Tar dehyd. #1 (AB) (1,2,3) Time Sampled 6:20
West

Sample Type: (Liquid) Air

Sample Temperature 207 °F

Ambient Temperature

Description of Sampling Location: dipped from manway

Sample No. Tar dehyd. #2 (NB) (1,2,3) Time Sampled 6:25
East

Sample Type: (Liquid) Air

Sample Temperature 219 °F

Ambient Temperature

Description of Sampling Location: dipped from manway

PROJECT 1906 BENZENE/BaP PRESURVEY

SAMPLE DATA

Plant USS Fairless Process Wash oil decanter Date 9/16/80

Sample No. Wash oil decanter #1,2,3 Time Sampled 4:40 pm

Sample Type: Liquid Air

Sample Temperature 205 °F

Ambient Temperature 87 °F

Description of Sampling Location: dipped from hatchway next to vent.

Sample No. _____ Time Sampled _____

Sample Type: Liquid Air

Sample Temperature _____

Ambient Temperature _____

Description of Sampling Location:

Sample No. _____ Time Sampled _____

Sample Type: Liquid Air

Sample Temperature _____

Ambient Temperature _____

Description of Sampling Location:

PROJECT 1906 BENZENE/BaP PRESURVEY

SAMPLE DATA

Plant Wh-Pitt McNESSEN Process LIQ-SAMPLES Date 8/13/80

Sample No. Tar inlet Time Sampled 2:55

Sample Type: (Liquid) Air

Sample Temperature 71 °C

Ambient Temperature

Description of Sampling Location:

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

Sample Type: (Liquid) Air

Sample Temperature 25 °C (ambient)

Ambient Temperature

Description of Sampling Location:

Sample No. Tar Storage Time Sampled 3:20

Sample Type: (Liquid) Air

mostly flushing liquor

Sample Temperature 75.5 °C

Ambient Temperature

Description of Sampling Location: dipped from manway on tank.

APPENDIX B

LIQUID SAMPLE ANALYSIS

Liquid Sample Analysis

Source/Plant	Sample Location	Date	Time	Sample Temp. (F°)	Benzene* Conc. (ppm-wt)
Tar Decanter (B)	Liquor on Surface	7/8/80	1525	176	5.6
		7/8/80	1600	180	4.2
Tar Decanter (BH)	Liquor on Surface	9/23/80	1525	120	181.6
					58.1
					35.5
Tar Dehydrator (BH)	Tar from Outlet Pump	9/23/80	1420	162	1956
					1834
					2171
Tar Storage (P)	Liquor on Surface	10/7/80	1700	145	16.8
					75.4
					6.2
Wash Oil Decanter (F)	Oil on Surface	9/10/80	1640	205	42.2
					40.3
					50.3
Tar Dehydrator-W (F)	Tar on Surface	9/11/80	1820	207	629
					599
					634
Tar Dehydrator-E (F)	Tar on Surface	9/11/80	1825	219	282
					286
					261

*Note: The three concentrations shown for most sources were obtained from three separate liquid samples collected consecutively.

APPENDIX C

LABORATORY HEADSPACE DATA

CHROMATOGRAPHIC ANALYSIS LOG

Project No. 1957 Date _____ Analyst _____

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	[illegible] Holder				
	Tan Decanter				
	[illegible]				
	Sample 1)	58.5	18.3	1070 x 10	10700 ppm
	2)	72			13160 ppm
	3)	72			13160 ppm
	Tan [illegible]				
	Sample 1)	61	18.3	1115.1 x 10	11151 ppm
	2)	74.5	18.3		13619 ppm
	Std 100.6 ppm 1x10²	22	4.57		

CHROMATOGRAPHIC ANALYSIS LOG

Project No. 1957 Date _____ Analyst _____

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	[illegible]				
	[illegible] 10x				
	9x10²				
	Sample 1)	15	9.36	140.4 x10	1404 ppm
	2)	14			1310 ppm
	[illegible] AB				
	[illegible] 10x 2x10⁴				
	Sample 1)	24	9.15	219.6	2196 ppm
	2)	28			2560 ppm
	[illegible] NB				
	[illegible] 2x10⁴				
	Sample 1)	33	9.5		3220 ppm
	2)	35			3200 ppm

Std 100.6 [illegible] 22

CHROMATOGRAPHIC ANALYSIS LOG

Project No._____ Date_____ Analyst_____

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	[illegible]				
	Tow Strong [illegible]				
	[illegible] 10x 4x10²				
	Sample 1)	16.5	10.32	171.9 x 10	1719 ppm
	2)	10.5			[illegible] ppm
	Std 100.6 ppm 1x10²	39			
	Tow [illegible] 8x10²				
	Sample 1)	57	23.67	[illegible]	[illegible] ppm
	2)	47	23.67		20250 ppm
	Std 100.6 ppm	[illegible]			

CHROMATOGRAPHIC ANALYSIS LOG

Project No._____ Date_____ Analyst_____

Time	Sample Identification	Peak Height/Area	Concentration Factor	Concentration	Comments
	CF+I Toe Stringer [illegible] 1 x 10[illegible]				
	Sample 1)	67	4.57	306 x 10	[illegible]
	2)	67			[illegible]