

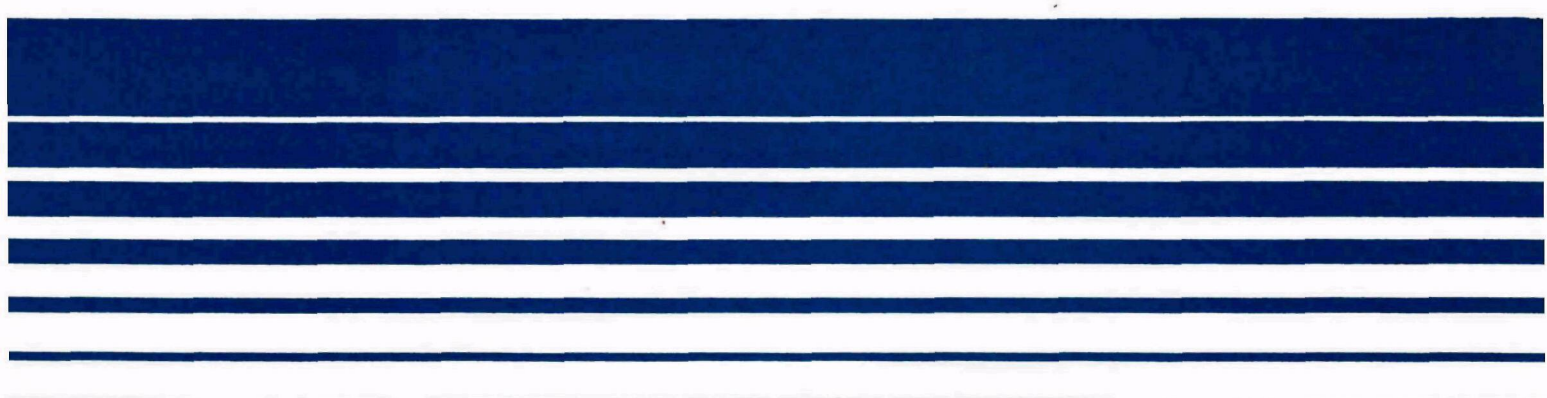
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# **Steel Industry By-Product Coke Ovens**

## **Emission Test Report U.S. Steel Corporation Clairton, Pennsylvania**



SOURCE TEST AT U. S. STEEL  
CLAIRTON COKE OVENS

CLAIRTON, PENNSYLVANIA

by

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## GLOSSARY

BaP - Benz-a-Pyrene  
BSO - Benzene Soluble Organics  
DSCM - Dry Standard Cubic Meters  
GC - Gas Chromatograph  
MeCl - Methylene Chloride  
MS - Mass Spectrophometer  
PAH - Polynuclear Aromatic Hydrocarbons  
POM - Polycyclic Organic Matter  
SASS - Source Assessment Sampling System

## SAMPLE LABELING GLOSSARY

CD - Module Condensate  
CICD - Impinger Contents  
CIMC - Methylene Chloride Impinger Rinse  
MR - Module Rinse Methylene Chloride  
NMC - MeCl Nozzle Rinse  
NPR - Nozzle Probe/Filter Rinse  
P - Combined Probe  
PF - Filter  
PIB - Probe/Impinger Benzene Rinse  
PICD - Probe/Impinger Condensate  
PR - Probe/Filter Rinse  
V - Vent Rinse  
VB - Benzene Vent Rinse  
VMC - Vent Rinse Methylene Chloride  
XR - XAD-2 Resin

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## 1.0 INTRODUCTION

During the week of July 30 through August 6, 1978, TRW Environmental Engineering Division, under Contract No. 68-02-2812, with the Environmental Protection Agency's Emission Measurement Branch, tested a battery of coke ovens at U.S. Steel's Clairton, Pennsylvania plant. The purpose of this sampling was two-fold: 1) to provide data associated with emissions of polycyclic organic matter from topside leaks and 2) to verify that a reduction in visible topside emissions would result in an emissions reduction of polycyclic organic material.

Sampling was conducted in order to determine the emission rate (mg/min) of pollutants from a simulated coke oven topside leak; two different size leaks were tested. In addition, background ambient samples were taken from battery topside. The leaks were simulated by modifying an oven port lid to include a vent tube which utilized a ball valve for controlling the leak rate. Samples were collected by placing the nozzle of the sampling train probe directly above the vent tube. Pollution emission rates were determined for Benzene Soluble Organics (BSO), Polycyclic Organic Matter (POM), and Benz-a-Pyrene (BaP); determination of a Benzene emission rate was attempted but was not successful.

## 2.0 SUMMARY

During the week of testing at the Clairton Coke Works, seven samples of BSO/POM were taken from the simulated oven leaks on Battery Number 1. In addition, two ambient air samples were taken at the battery topside to provide information on the background pollutant level. During each run the simulated leak was adjusted to give either a large leak (approximately a three to six-foot visible plume) or a small leak (approximately a one-foot visible plume). Tests one through four were taken during a large leak while tests five through seven were taken during a small leak. Photographs of the sampling apparatus and the simulated leaks were taken during the test program for EPA by U.S. Steel personnel; these photographs are on file at the EPA. All sampling was done on the number one coke oven battery at the Clairton Plant. In order to minimize problems with taking the sampling equipment onto the hot battery topside, the ovens closest to the pinion wall were selected for testing. In all cases, the oven lid closest to the push side of the battery was used. Sampling was begun between the first and second hours after the oven was charged. The ambient samples were taken on battery topside past the pinion wall (i.e., between oven A-1, and the end of the battery); this position was approximately 40 feet from the simulated leak. A more detailed discussion of the sampling locations is presented in Section 5. A Summary of Results are shown in Table 2.1.

Separate sampling trains were used for the BSO and the POM/BaP sampling. In order to obtain comparable BSO/POM data, a common nozzle was used so that both trains could simultaneously sample the same leak. The sampling rates were adjusted so that approximately half of the leak went to each train. Both trains were of a modified Source Assessment Sampling System (SASS); SASS trains were used in order to obtain a high sample rate.

SUMMARY OF RESULTS

TEST RUN	TEST TIME	DATE	OVEN NUMBER	LEAK SIZE	BSO				POM				BAP	
					SAMPLE TIME (min)	MASS COLLECTED (mg)	EMISSION RATE (mg/min)	VOL. SAMPLED (DSCM)	SAMPLE TIME (min)	MASS COLLECTED (mg)	EMISSION RATE (mg/min)	VOL. SAMPLED (DSCM)	MASS COLLECTED (mg)	EMISSION RATE (mg/min)
1	12:50	6/2	A III	Large	24	784	32.68	1.664	30			1.873		
2	14:23	8/2	A I	Large	6	1700	283.33	0.118	9			0.131		
3	8:35	8/3	A V	Large	15	8819	587.93	1.069	15			0.637		
4	10:16	8/3	A VII	Large	8	1618	202.25	0.148	10	2189	218.9	0.404	35.83	3.58
5	12:53	8/4	A II	Small	16	458	28.63	0.672	15			0.823		
6	21:32	8/4	A I	Small	15	714	47.60	0.730	15			0.880		
7	16:45	8/5	A I	Small	15	1312	87.47	0.604	15	511	34.0	0.803	17.91	1.19
5A	12:33	8/4	Ambient	None	56	9.3	0.084	9.988	55			9.608		
5B	21:12	8/4	Ambient	None	55				55					
7A	15:07	8/5	Ambient	None	70	9.0	0.128	6.709	69	7.6	0.11	6.347	0.12	0.0017

5A Collected During Run 5

5B Collected During Run 6

Table 2.1. SUMMARY OF RESULTS

## POLYCYCLIC ORGANIC MATERIAL ANALYSES

COMPOUND	MOLECULAR WT.	BAP 4		BAP 7		BAP 7A	
		MASS (mg)	EMISSION RATE (mg/min)	MASS (mg)	EMISSION RATE (mg/min)	MASS (mg)	EMISSION RATE (mg/min)
NAPHTHALENE	128	320.2	32.0	138.8	9.2		
BIPHENYL	154	13.6	1.4	3.1	0.2		
DIMETHYLNAPHTHALENES	156	10.1	1.0	1.6	0.1		
ACENAPHTHYLENE	152	128.8	12.9				
DIBENZOFURAN	168	71.8	7.2				
FLUORENE	166	81.0	8.1	15.4	1.0		
DIMETHYLBIPHENYLS	182	18.3	1.8				
DIBENZOTHIOPHENE	184	21.2	2.1	2.0	0.1		
PHENANTHRENE	178	374.0	37.4	55.2	3.7	3.1	0.045
BENZO(h)QUINOLINE	179	4.4	0.4				
CARBANZOLE	167	44.9	4.5				
METHYLPHENANTHRENE	192	33.8	3.4	4.3	0.3		
4H-CYCLOPENTA (def) PHENANTHRENE	190	32.0	3.2				
PHENYLNAPHTHALENE	204	9.2	0.9				
PYRENE	202	153.8	15.4	31.9	2.1	1.4	0.020
FLUORANTHENE	202	146.2	14.6	30.0	2.0	0.7	0.010
BENZO(a)FLUORENE	216	26.6	2.7	5.9	0.4		
METHYLPYRENES	216	46.2	4.6	10.2	0.7		
BENZO(ghi)FLUORANTHENE	226	9.8	1.0				
CHRYSENE	228	8.5	0.8	65.9	4.4		
BENZO(a)ANTHRACENE	228	150.0	15.0				
TERPHENYL	230	5.4	0.5				
METHYLBENZOANTHRALENES	242	29.4	2.9	10.6	0.7		
BENZOTHIOPHENE	240	18.7	1.9				
BENZOPYRENES	242	296.1	29.6	135.7	9.0		
BENZOPERYLENES	276	109.8	11.0			2.4	0.035
DIBENZOANTHRACENE	278	24.7	2.5				
TOTAL POM		2188.5	218.8	510.6	33.9	7.6	0.110

TABLE 2.2. POM ANALYSIS



The BSO fraction was passed through a dry impinger into a filter at 125<sup>0</sup>F. The filter and first impinger contents were extracted with benzene; the extract was dried and the BSO determined gravimetrically. The filtered gas flow proceeded through three more impingers containing water and finally through silica gel before being measured at the meter box. The impingers were extracted with benzene which was dried and weighed.

The POM/BaP fraction was collected on a filter at 125<sup>0</sup>F and a solid adsorbent resin (XAD-2) which were both extracted with methylene chloride (MeCl). The gas then passed through a series of impingers containing water and silica gel before being measured on the gas meter. The recovered water was extracted with MeCl. POM analysis was conducted on a Gas Chromatograph/Mass Spectrometer (GC/MS) - by TRW's West Coast Analytical Department. The BaP analysis was conducted at the EPA's Research Triangle Park location by thin layer chromatography/fluorescence. Only runs 4, 7 and 7A were analyzed for POM/BaP. For the remaining runs the samples were extracted and the extract retained for possible future analysis.

An integrated bag was taken after the filter from the BSO stream. It was analyzed on-site for benzene with a gas chromatograph. The benzene results are missing from this report since it was determined that the high concentrations of the volatile organic matter present in the sample made the determination of benzene impossible. The gas chromatography column utilized in the field on the integrated bag sample did not perform an adequate separation of benzene from the interfering compounds.

### 3.0 DISCUSSION OF RESULTS

Upon arrival at the plant the van was set up next to the coke ovens. Generators were rented in order to provide power for the SASS trains. The vent pipe was placed on an oven lid. The orifice plate (Section 6) in the vent pipe not only caused a flow restriction but also provided a flat surface on which tar formed a viscous layer resulting in complete plugging of the vent in a short period of time. The orifice plate was removed and a larger steadier flow resulted. All tests were conducted without an orifice plate. Prior to the first run a problem was encountered with plugging of the leak vent which seemed to be caused by particles of coal fines. A new vent was placed on the lid and the first test conducted. Although the leak vent did not totally plug during the test, the flow appeared to be somewhat restricted. The determination was made that this problem of flow restriction due to coal fines would occur only during the first hour of testing, therefore subsequent tests were begun one hour after oven charging. The partial plugging of the vent is reflected in the results. The first test was of longer duration (24 minutes) and collected less mass than the subsequent tests at the large leak rate. The first test was considered an experiment and three more complete tests were conducted. During the sampling the probe nozzle was placed one half inch above the vent outlet to permit visual monitoring of the leak. The observation of the leak assured that plugging of the vent did not occur during the tests runs.

SASS trains were used to collect the sample. The POM/BaP train and the BSO train used a common nozzle which was placed above the simulated leak. After a photograph of the leak was taken, the test was initiated. The pumping rate was adjusted so that each train

sampled an equal amount and the entire leak was captured. The tests were of a short duration due to the plugging of the filters on each train. The runs were discontinued when the filters were overloaded. The flow rates were adjusted by timing the volume and observing the meter orifice pressure differential. This was not an accurate process; therefore, the volumes collected were not exactly equal. The valve that adjusted the leak was a coarse ball valve which only permitted approximately the desired leak rate. The variability in the leak rate accounted for the different sampling times.

The filter was placed on the wrong side of the supporting screen during run 3 in the BSO train. This accounts for the large sampling volume and mass collected. The sample volumes of run 4 disagree by a factor of four. No apparent reason is known for this other than they were both low volumes and this type of variance in flow rate could easily have resulted from the flow approximating method.

Methylene chloride was to have been used as an impinger solvent, however, during the first attempted leak check it was found to be freezing the impingers at the tips and causing plugging. Water was substituted and used in all the tests.

The ambient trains were operated approximately 40 feet away from the oven lids. The ambient test runs were started before the BSO/POM tests and were stopped after the sampling. Duration and volume sampled were greater than the lid leak tests in an attempt to produce a measureable sample.

Immediately following each test the samples were recovered. The recovered samples were transported to TRW's west coast facilities where the splitting, combining, extraction and analysis took place. MeCl was used to rinse the sampling equipment as well as for the extraction of the POM train filter and Resin. The complete results of the GC/MS analysis are contained in Appendix B. Only samples 4, 7 and 7A were analyzed for POM/BaP. The sample splits of these samples were sent to EPA at Research Triangle Park, North Carolina. Where thin layer chromatography /spectroscopy for Benz-a-Pyrene analysis were performed. These results are listed in Appendix B. For all other runs the samples were extracted and the extract retained for possible future analysis.

During testing, an integrated bag was collected from the BSO train after the filter. This bag was analyzed on site for benzene utilizing an OV-101 column on a dual flame ionization detector gas chromatograph. The resulting chromatogram displayed numerous peaks in the retention time frame of benzene. These peaks made it impossible to discern which peak was benzene or if benzene was masked by the interfering peaks. Although different column conditions were attempted, the high concentrations of volatile organic matter present in the sample rendered separation impossible. No benzene results are presented here.

Multiple extractions were performed on the BSO samples (filter) to determine the efficiency of the first and subsequent extractions. The average of the first extractions were 98.8% of the total with the remaining 1.2% present in the second extraction. No weight gains were recorded for the third extraction. Complete results are listed in Appendix B. Multiple extractions with Methylene chloride were conducted on filters and resins for several POM samples in order to determine the efficiency of extraction. The first extraction contained 99.9% of the measurable POMs and the second extract the remaining 0.1%. The third extractions were below detection limits. Furthermore, cyclohexane extractions were conducted on several samples after the MeCl extraction to determine the efficiency of the MeCl extraction. The BaP cyclohexane extractions were below the detection limits.

#### 4.0 PROCESS DESCRIPTION

Battery 1 is one of three batteries (1, 2, 3) of a coke oven operating facility located at the Clairton works. Table 1 lists design parameters of Battery 1.

During the testing, Battery 1 was operated in a normal manner. The average gross coking time was 18 hours. Table 2 lists the production rates for each day of testing. Table 3 lists coal analyses (conducted by U.S. Steel) for each day of testing.

TABLE 1  
COKE OVEN BATTERY DESCRIPTION<sup>1</sup>

Type	Wilputte
Number of ovens	64
Date of initial operation	1918
Date of last pad up rebuild	1955
Approximate oven width (average)	18.5 inches
Approximate oven height (floor to roof)	11 feet 10 inches
Approximate oven length (between doors)	37 feet 4 inches
Free space above coal	13 inches
Calculated capacity (cubic foot coal)	626
Charging holes	4 per oven
Charging hole diameter	18 inches
Number of collecting mains	2
Type of oven doors	self-sealing
Type of charging	gravity feed stage charging

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<sup>1</sup> Information from letter of September 6, 1974 from John G. Munson, Assistant to Vice President of U.S. Steel, to Reid Iversen, EPA.

TABLE 2  
PRODUCT INFORMATION

<u>Date</u>	<u>Ovens Charged Per Day</u> <sup>1</sup>	<u>Gross Coking Time (hrs)</u>
8/1/78	81	19.0
8/2/78	83	18.5
8/3/78	73	21.0
8/4/78	83	18.5
8/5/78	82	<u>18.7</u>
		19.1

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<sup>1</sup> Information from letter of September 18, 1978 from R.J. Weiskircher of U.S. Steel to C.E. Riley, U.S. EPA.

TABLE 3: COAL ANALYSIS<sup>1</sup>

	%H <sub>2</sub> O	%Sulphur	%Ash	%Volatiles	Screen Size			
					+ .500 inch	+ .250 inch	+ .125 inch	- .125 inch
8/1/78	6.5	1.15	7.45	28.80	4.6	14.8	17.1	63.5
8/2	6.3	1.21	7.75	28.75	3.0	14.9	16.3	65.8
8/3	6.2	1.14	7.65	29.60	4.3	13.6	16.7	65.4
8/4	5.9	1.15	7.80	29.40	5.7	14.2	15.4	64.7
8/5	6.8	1.16	8.25	29.15	4.7	15.0	15.3	65.0

<sup>1</sup> Information from letter of September 18, 1978 from R.J. Weiskircher of U.S. Steel to C.E. Riley, U.S. EPA.



## 5.0 LOCATION OF SAMPLING POINTS

All sampling points were located on the topside of the number one coke oven battery at the Clairton Works. The oven charging port closest to the push side was chosen for sampling. One end of the oven battery was chosen because it would least disturb the normal operation of the charging trolley. All samples were taken from ovens  $A_1$  through  $A_7$ , depending upon the daily charging sequence. The ambient samples were taken from topside at a location past the pinion wall. Figure 5.1 is a schematic of the battery topside indicating the sampling locations.

● → SAMPLE POINT

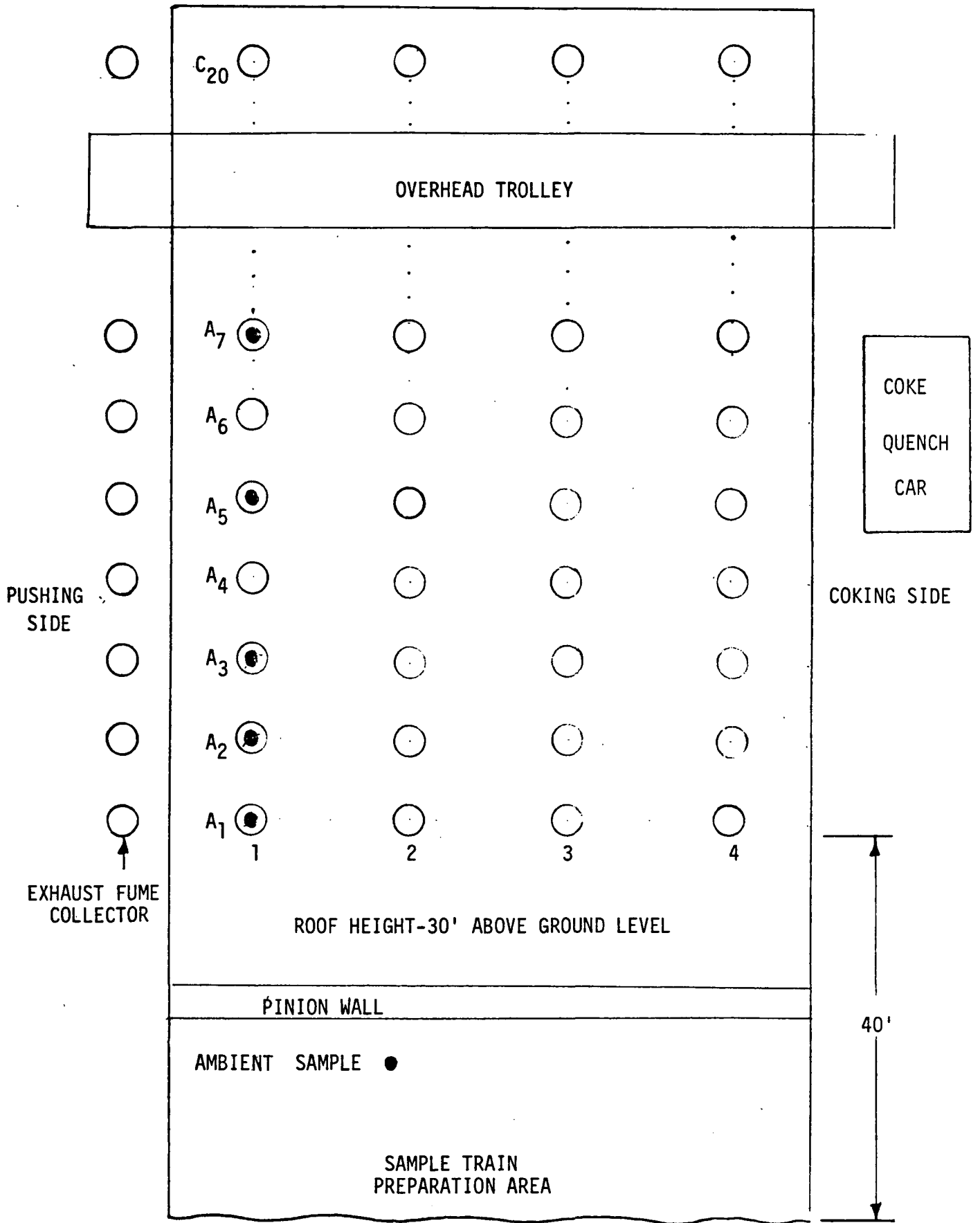


FIGURE 5.1 : BATTERY 1 (TOPSIDE VIEW)

## 6.0 TEST PROCEDURES

During the testing, the oven was charged with the overhead trolley and the lids replaced and sealed by U.S. Steel personnel; a special lid modified with a valve and vent pipe was replaced on one of the oven ports (see Figure 6.1). After the lids had been sealed, a simulated leak was attempted at the desired plume length. Condensation occurred in the vent forming a viscous substance; consequently, the plume was monitored continuously to assure clogging of the vent did not occur. Once the plume was determined to be the correct size, the nozzle was placed over the vent and the sampling trains were started. During sampling, the vent was visually monitored continuously to assure that the sampling rate was sufficient to assure total capture of the leak. Sampling was continued until plugging in the vent occurred or until the loading on the sample train filter caused an excessive decrease in the sampling rate. The sampling rates of the BSO and POM sampling systems were evenly maintained in order to evenly split the sample between the two trains.

The sampling was conducted in accordance with the draft methods--Determination of Benz-a-Pyrene Emissions from Stationary Sources and Determination of Benzene Soluble Organics. Both of these methods were supplied by EPA and both are draft procedures. Several exceptions to the procedures of these Methods were made. SASS sampling trains were substituted for the regular Method 5 trains and the two sampling trains shared a common nozzle (see Figure 6.2). The ambient air sampling system was a Method 5 train modified to accept the XAD-2 adsorbing module; no nozzle was used for this train. Methylene chloride was not used in the impingers because of a problem in freezing due to the heat loss inherent in volatile organic compounds. This was determined during the first run. Subsequent impinger fractions used water as a collection

medium. Methylene chloride was used for cleanup and extraction of the POM train in lieu of cyclohexane.

The basic sample train components are diagrammed in Figure 6.3. All the components used were standard source assessment sampling system (SASS) parts. A simulated leak was created by the pressure in the oven flowing through the valve to the atmosphere. After visually measuring the leak a nozzle common to both trains was positioned over the leak. The nozzle was not connected but just positioned over the leak. The train's pumps were adjusted to provide approximately half the leak to each sample train. Some excess air was also sampled to insure all of the vent gases were captured. The probe and heated oven were maintained at 125<sup>0</sup>F for the BaP/POM train while only the probe was heated to 100<sup>0</sup>F for the BSO train. The BaP/POM train filtered the sample to remove the particulate matter. The non-particulate gases were then collected by passing the gas sample through an XAD-2 absorbent resin maintained at 70-90<sup>0</sup>F. Cooled impingers and silica gel were used to collect the remaining moisture prior to the pumps and the gas flow meters. The BSO train collected the particulate in the first impinger and on the filter. A dry impinger was placed prior to the filter in order to minimize plugging. During the sampling, an integrated Tedlar bag was taken after the impingers but before the silica gel on the BaP/POM train. A sample identification log is contained in Appendix C. This log lists each sample fraction and the solvent used in clean up and recovery. They are generally shown in the following table. The GC/MS analysis was performed according to the procedures outlined in Analysis of Polynuclear Aromatic Hydrocarbons from Coke Oven Effluents by R. E. Beimar, September, 1978 (EPA report 78-CKO-12). The Column utilized was a Dexcel 300 packed column for the separation of POMS!

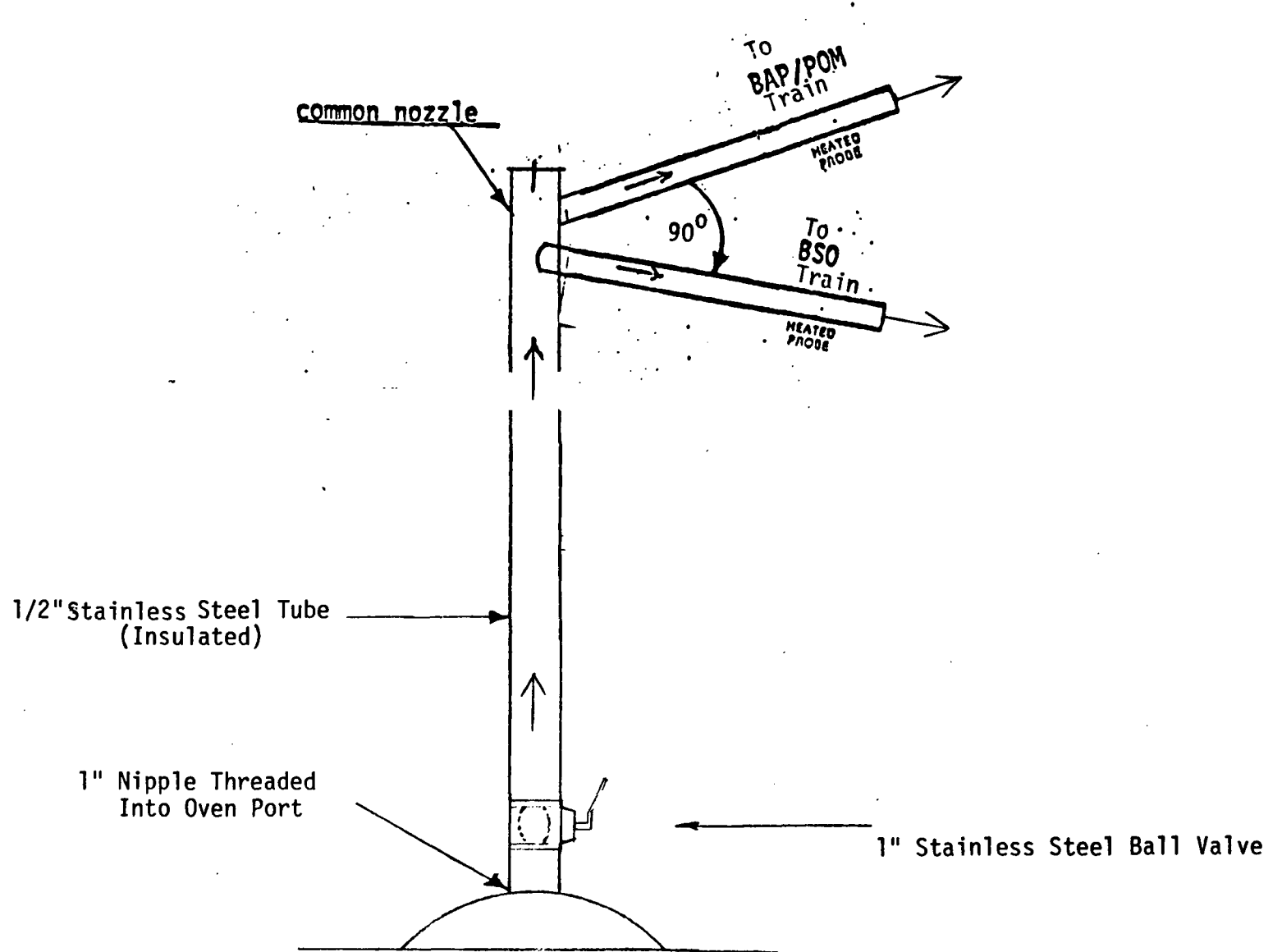


Figure 6.1 Sampling Vent/Probe Configuration

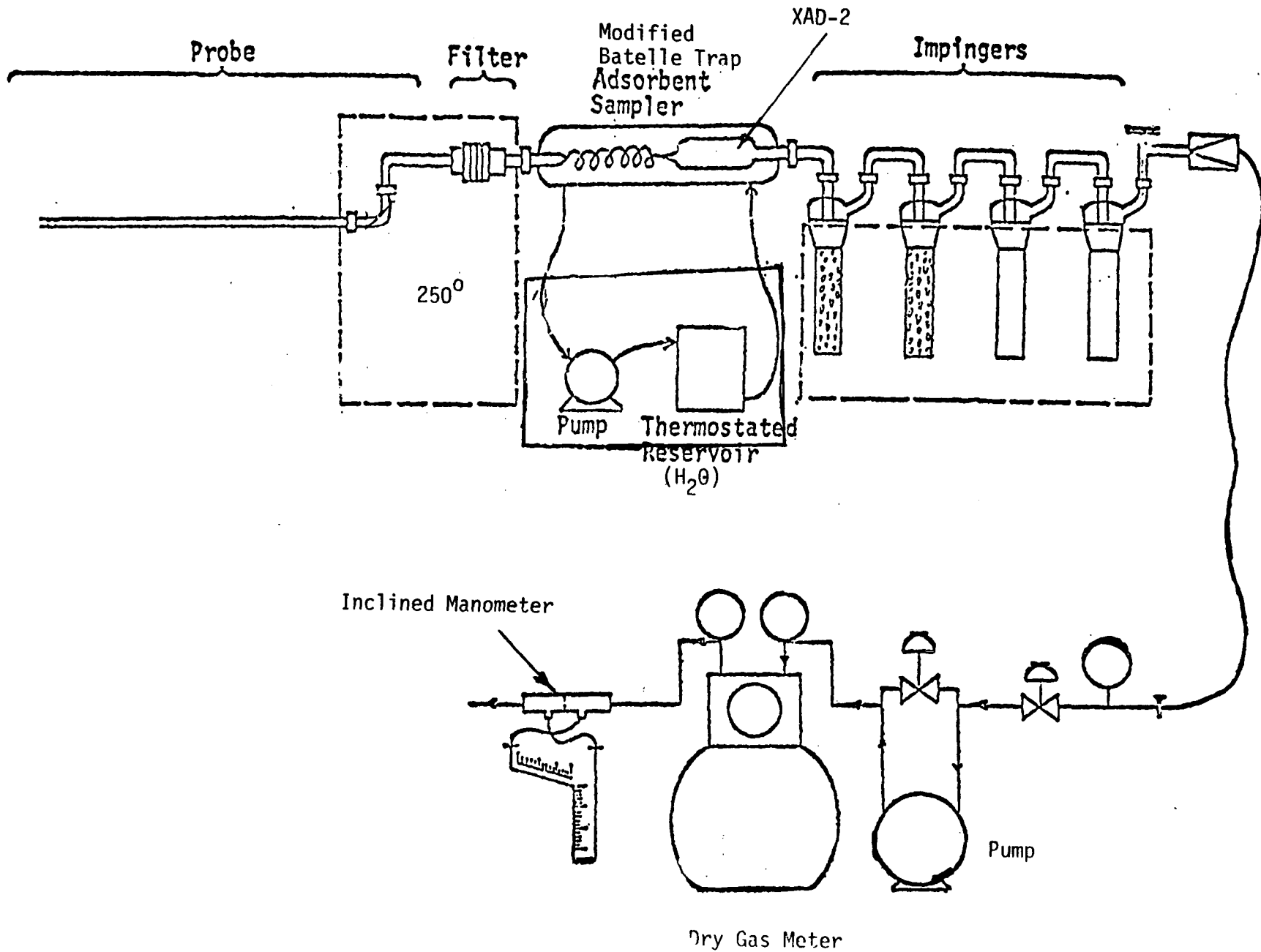


FIGURE 6.2 AMBIENT TRAIN

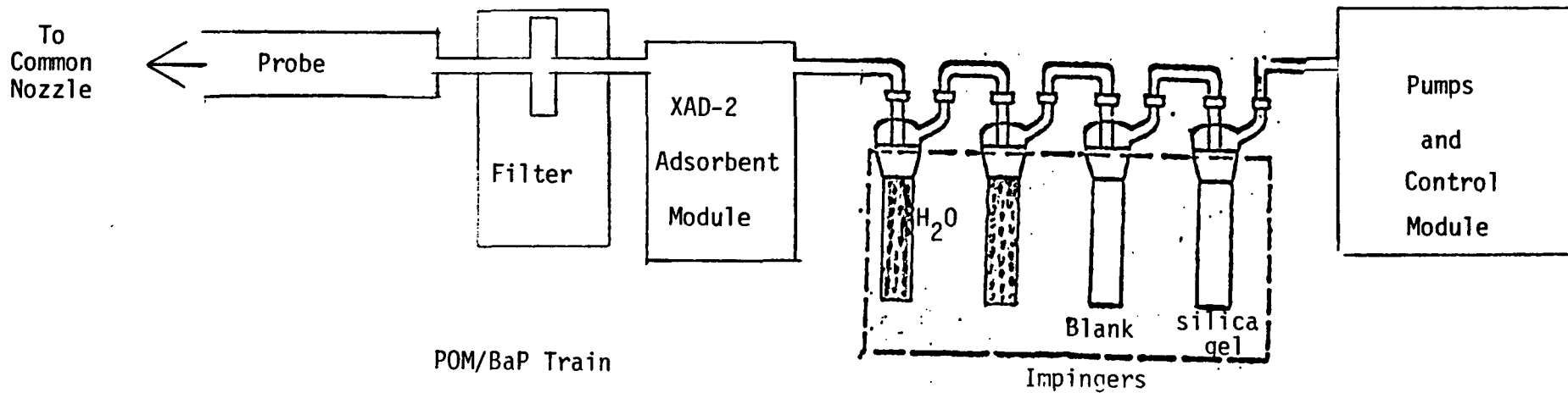
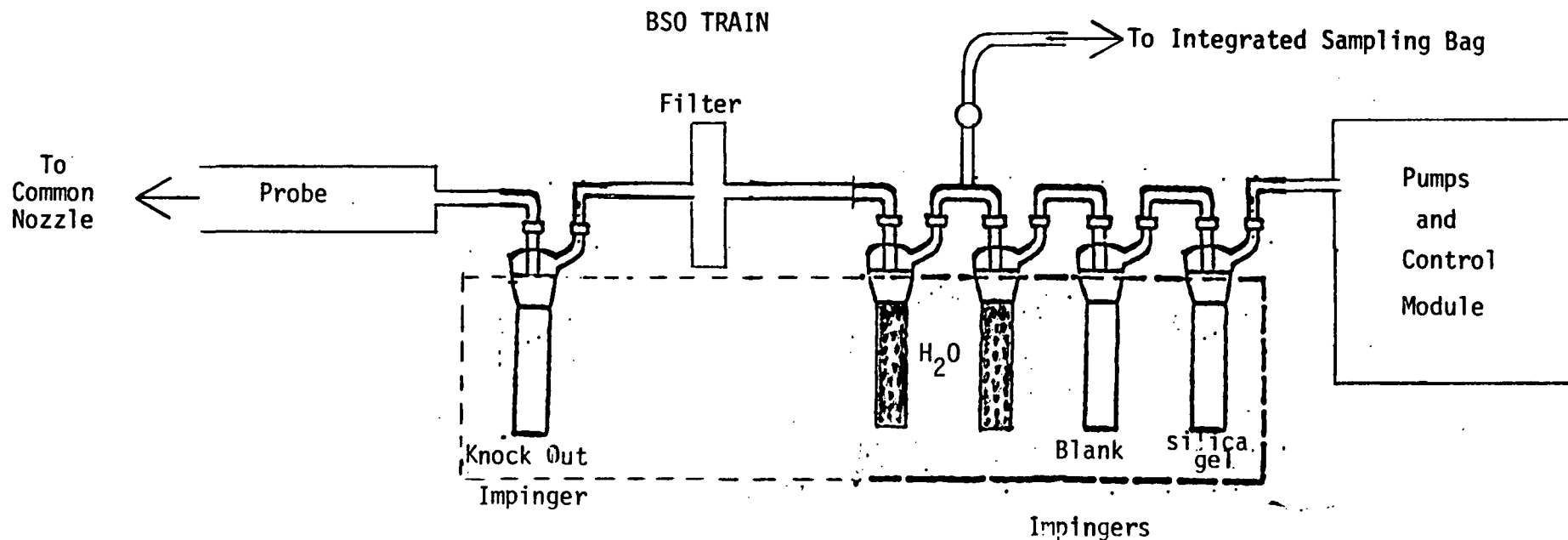


Figure 6-3. SASS SAMPLING TRAINS

### Field Recovery of BSO Train

<u>Component</u>	<u>Recovery Steps</u>
Probe, Knock-out Impinger, Filter Housing	Condensate collected Acetone Rinse Benzene Rinse
Filter	Collected
Impingers <sup>1</sup>	Condensate collected Acetone Rinse Benzene Rinse

### Field Recovery of BSO/BaP Trains (Common Components)

<u>Component</u>	<u>Recovery Steps</u>
Vent Pipe	Methylene Chloride Rinse Benzene Rinse
Common Nozzle	Methylene Chloride Rinse Benzene Rinse

### Field Recovery of BaP Train

<u>Component</u>	<u>Recovery Steps</u>
Probe, Front of Filter Holder	Methylene Chloride Rinse
Filter	Collected
XAD-2 Resin	Collected
Back of Filter Holder and Module	Condensate Collected Methylene Chloride Rinse
Impingers <sup>1</sup>	Condensate Collected Acetone Rinse Methylene Chloride Rinse

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<sup>1</sup>Some Impingers contained activated charcoal which was not recovered after each test. The same is true of the silica gel.



Laboratory Sample Preparation  
(BaP/BSO Common Fractions)

1. Nozzle - Methylene Chloride Rinse - Split<sup>1</sup>  
Benzene Rinse - Split<sup>1</sup>
2. Vent - Methylene Chloride Rinse Split (A,B,C)  
Benzene Rinse

Laboratory Sample Preparation  
(BSO Fractions)

1. Nozzle Benzene Rinse<sup>3</sup>, Probe, and  
Knock-out Impinger Benzene Rinse  
and Nozzle Methylene Chloride Fraction<sup>2</sup> Combined and Split<sup>4</sup> (D,E)
2. Probe Knock-out Impinger Acetone Rinse - Split (D,E)
3. Filter Benzene Extraction and Split (D,E)
4. Impinger Liquid - Split (D,E)
5. Impinger Acetone Rinse - Split (D,E)
6. Impinger Benzene Rinse - Split (D,E)
7. Knock-out Impinger Condensate - None in most cases

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<sup>1</sup>The rinses split in a ratio to correspond to the sampled gas volumes of the BaP/BSO trains for each test.

<sup>2</sup>Nozzle fraction (Methylene Chloride) after being brought to dryness and re-extracted with Benzene.

<sup>3</sup>Nozzle fraction derived from the BaP/BSO common fractions.

<sup>4</sup>The samples were split in half. The "D" fractions were dried and weighted gravimetrically by TRW. The "E" fractions were sent to EPA and from EPA to U. S. Steel.

