PHASE III SURVEY REPORT #5

WORKER EXPOSURE TO POLYAROMATIC HYDROCARBONS AT SELECTED PETROLEUM REFINERY PROCESS UNITS

LOCATION OF SURVEYS:

GULF OIL REFINERY
PHILADELPHIA, PENNSYLVANIA

Dates of Surveys:

12-14 DECEMBER 1978
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ABSTRACT

A Gulf Oil refinery was surveyed during Phases I, II, and III of this NIOSH-sponsored study characterizing worker exposure to suspected carcinogens in petroleum refineries. Phase I included a walk-through industrial hygiene survey of the entire refinery accumulating information related to occupational health and to specific process units. In the Phase II survey, area air samples were collected at the two catalytic crackers and the deasphalting unit for polyaromatic hydrocarbons (PAHs), aromatic amines, trace metals, nickel carbonyl, and nitrosamines. The PAHs were the only group of compounds that were consistently found in the area samples.

In the Phase III survey, personal and area air samples were collected for PAHs in one of the catalytic crackers (one not operating) and the deasphalting unit. A silver-membrane filter followed by Chromosorb 102 was used for sampling, and analysis for 23 individual or groups of PAHs was performed by gas chromatography/mass spectrometry. All 25 of the personal and area air samples had detectable quantities of at least four PAHs or groups of PAHs with the cumulative PAH concentration for individual samples ranging from 2.0 $\mu g/m^3$ for a personal sample from one of the operators at the catalytic cracker to as high as 202.2 $\mu g/m^3$ for one area location in the same unit. The upwind boundary samples were both less than 1 $\mu g/m^3$.

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I. INTRODUCTION

Enviro Control, Inc. (Enviro) is under contract to the National Institute for Occupational Safety and Health (NIOSH) to perform a study entitled, "Industrial Hygiene Characterization of Petroleum Refineries." Because petroleum refining is a complex industry involving such a large number of potentially hazardous agents, the study was structured in four progressive phases to enable the development of a meaningful yet manageable study plan. The first two phases of this study have already been completed with the information and resulting recommendations having been presented in the Phase I report (April 1979) and the Phase II report (November 1979). Following is a brief description of these two initial phases as well as descriptions of Phase III and Phase IV.

- Phase I: A detailed literature search was performed including the industrial hygiene aspects and the potential occupational health problems associated with this industry. Preliminary fact-finding surveys were conducted at three refineries. This phase culminated in a preliminary study protocol which recommended the investigation of potential carcinogens in three types of refinery process units: the fluid catalytic cracker unit (FCCU), the delayed coker unit, and the asphalt processing unit.
- Phase II: Refinery surveys were conducted to identify specific compounds associated with some degree of cancer-causing potential in the three study process units. Area air samples were collected for a variety of compounds at three refineries, two of which were visited previously during Phase I. Results consistently showed the presence of polyaromatic hydrocarbons (PAHs) in the three study process units.

- Phase III: The objective of this main phase of the study is to characterize worker inhalation exposure to PAHs in the three study process units. Personal and area air samples will be collected in a total of nine refineries.
- Phase IV: A final report will be prepared integrating the results and information from Phase III and the previous phases.

The Gulf Oil refinery, located in Philadelphia, Pennsylvania, was one of only two refineries that were visited during each of the first three phases of this project. This report presents the information and air sampling data collected during those three surveys.

The Phase I survey was conducted from December 12 to 14, 1978. This was the first of three walk-through surveys conducted during this phase to gather information to be used in preparation of the project study protocol. An opening conference was held the first day with representatives from the refinery, the refinery's corporate office, NIOSH, and Enviro (list of attendees in Appendix). The three representatives from Enviro and the NIOSH Project Officer described the project and the specific objectives of the survey; a tentative schedule for the 3 days was agreed upon, whereby the Enviro industrial hygienists could see as much of the refinery as possible. The third day included limited direct-reading and long-term air sampling at selected process units. At the end of the survey, a closing meeting was held with the refinery personnel to answer questions and establish a procedure for future interaction. The arrangements for this visit were made through the refinery manager and director of accident and fire prevention.

The Phase II survey to this refinery was conducted on April 10-12, 1979. The objective of this survey was to collect a series of air samples for PAHs, aromatic amines, trace metals, nickel carbonyl, and nitrosamines in the two FCCUs and the solvent decarbonizer (deasphalting) unit. A brief opening conference was held the first day with representatives from the refinery, the refinery's corporate office, NIOSH, and Enviro (list of

attendees in Appendix). Enviro's representative explained the status of the project and the specific objectives of this phase; a tentative schedule was agreed upon for the 3 days. After the opening conference, the survey team conducted a walk-through of the three study process units. Both FCCUs were sampled during day shifts of the second and third days while the deasphalting unit was sampled during the day shift of the third day only. Thirty-seven (37) area samples were collected over the 2 days for the various compounds. All arrangements for this visit (and the Phase III visit) were made through the corporate industrial hygienists.

This Gulf Oil refinery was revisited on April 1-3, 1980, as part of Phase III of this project. The objective of this survey was to monitor worker exposure to PAHs at the same three process units studied in the previous phase through a program of personal and area sampling. However, one of the FCCUs was not operating during the survey and was not included. After a short opening conference on the first day (list of attendees in Appendix), the survey team conducted a brief walk-through of the two process units to be sampled. At both the FCCU and the deasphalting unit, the Enviro industrial hygienists explained to the employees the sampling to be performed. Sampling was conducted during the day shifts of the second and third days.

II. REFINERY DESCRIPTION

This Gulf Oil refinery, located in Philadelphia, Pennsylvania, is along the bank of the Schuylkill River in the southern part of the city. With its crude capacity of about 210,000 bbl/day, this refinery is classified as a "large" refinery for the purposes of the study. Since Gulf Oil is one of the 15 largest companies in terms of crude capacity, the company is considered a "major" oil company. The significance of categorizing this refinery by these criteria is explained in the Phase II report.

This refinery, which was built in 1924, is currently spread over approximately 600 acres. At the time of the Phase I and Phase II surveys, the refinery was operating at close to capacity; during the Phase III survey, it was operating at considerably less than capacity due to the turnaround on one of the FCCUs. A full line of petroleum products is produced including:

- propane
- butane
- gasolines (three grades)
- jet fuel
- fuel oils (#2, #6)
- lube oils
- petrochemicals (benzene, toluene, cumene)
- sulfur

The crude refined here, which is primarily Nigerian and Libyan, is categorized as a "light," "low-sulfur," "mixed base" (containing both paraffins and naphthenes) crude. Occasionally some North Sea crude (1% sulfur by weight) is also refined here. All of the crude is received by tankers which unload at a nearby docking station. The petroleum products produced here serve 11 nearby states. The products are transported primarily by ship and tank trucks.

The major process units at the Gulf refinery include:

- two atmospheric and vacuum distillation units
- solvent decarbonizer (deasphalting unit)
- two gulfiners (desulfurizing units)
- two catalytic reformers (platformers)
- two FCCUs
- HF alkylation unit
- lube extraction unit
- sulfur recovery unit
- dehazer unit
- benzene/cumene unit

Figure II-1 shows a rough plot plan of the main production area which is located in the northwest section of the refinery. Almost every major process unit has its own control room.

There is an approximate total of 1,350 employees; this includes 175 supervisory, 100 administrative, 360 maintenance workers, and 715 production workers. Most of the routine maintenance activity is performed in-house; a number of contractors are normally on the premises for other major maintenance work including turnarounds. The production units operate 24 hours a day, 7 days a week. There are normally four work crews that rotate on a unit. Both 8-hour and 12-hour shifts are used depending on the unit.

The refinery safety department consists of the Supervisor of Accident and Fire Prevention and three safety inspectors. The refinery also has a fully-equipped fire department staffed by nine firemen. Industrial hygiene services are primarily provided by the corporate industrial hygiene staff; five corporate industrial hygienists have responsibility for Gulf's eastern region. Industrial hygiene sampling for benzene is conducted here on a quarterly basis; the Supervisor indicated that there were no problems at this refinery with the current benzene worker exposure standards. Other monitoring at this refinery is conducted for compliance purposes (e.g., noise, lead), on an as-needed or request basis (e.g., detector tubes for ammonia, sulfur compounds), or for any other reasons deemed necessary by the refinery or corporate

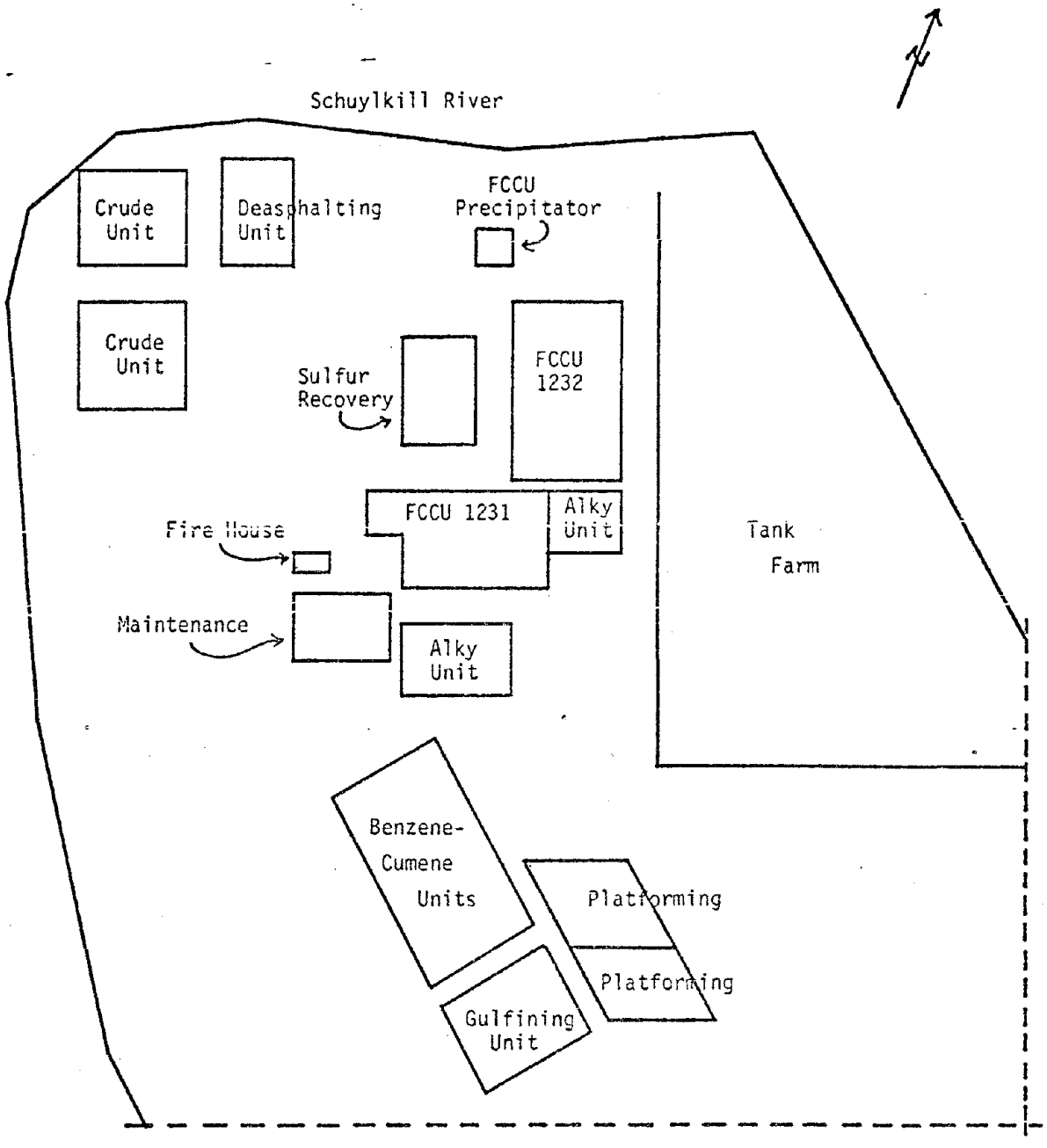


FIGURE II-1. Refinery Production Area

personnel (e.g., total hydrocarbons with direct-reading instruments, charcoal tubes for alkanes). Two refinery safety inspectors are trained to perform routine monitoring, and the corporate industrial hygienists also make periodic surveys.

As part of good industrial hygiene practice, the use of protective clothing and equipment (e.g., hard hats, safety shoes, gloves, eye protection) is emphasized with strict requirements in acid and caustic areas. While eating is allowed in most control rooms, smoking is permitted only in designated areas away from the production units. All new employees attend an extensive training session which includes information on unit equipment, operations, respirator use, safety hazards, fire protection, and first aid. The practice of good personal hygiene such as the washing of hands before eating is also encouraged; shower and locker facilities are provided at several refinery locations. Good unit housekeeping is practiced as an important means of minimizing worker exposure to potential hazards. Spills are promptly cleaned up by the unit operators and any necessary equipment or structure repair is promptly carried out by the unit operators or in-house maintenance crews.

The refinery employs a physician and two nurses who work out of the dispensary in the main administrative building. All employees receive preemployment medical examinations, and most production workers also receive yearly examinations. Approximately 150 refinery personnel are formally trained in first aid including cardiopulmonary resuscitation.

III. PHASE I

The objective of this initial walk-through visit to a large refinery was to gather information related to occupational health and to specific process units. During the first and second days, the survey team split up to enable walk-throughs of each of the major process units, the maintenance building, and the lube oil compounding, packaging, and shipping facilities. Interviews were also conducted with a process engineer, a nurse, and a member of the employee health and safety committee. All of this information contributed to the development of the study protocol which was presented in the Phase I Report (April 1979). This information was also used for various sections of this report, especially that regarding the refinery description (Chapter II).

Limited air sampling was conducted at selected process units during the third day of the survey to identify potential hazards and to establish concentration ranges. Detector tubes, an H-nu Photoionization Analyzer (Hnu), and a small number of charcoal and silica gel tubes were used. The Hnu detects all species with an ionization potential greater than 10.2 eV; this includes many aromatic hydrocarbons, organic sulfur compounds, olefins (except ethylene), amines, chlorinated hydrocarbons, aldehydes, and ketones. Table III-1 presents the semiquantitative area sampling data obtained using the direct-reading instruments. The weather conditions at 0600 of the sampling day were 33°F (1°C), 51% relative humidity, with winds out of the west at 13 mph gusting to 16 mph; at noon it was 37°F (3°C), 35% relative humidity, with winds out of the west-northwest at 25 mph gusting to 34 mph.

In addition to this direct-reading monitoring, several area air samples were collected at the crude distillation unit (#136), the FCCU (#1231), and the platformer (#1332) units using charcoal and silica gel tubes. A

TABLE III-1. Results of Direct-Reading Area Monitoring

PROCESS UNIT	LOCATION	Hnu OR TYPE OF DETECTOR TUBE	RESULTS (DETECTION LIMIT)
Crude distillation (#136)	control room	Hnu	neg (~1 ppm[1]) [2]
		hydrocarbon	neg (3.6 mg/ℓ)
		benzene	neg (5 ppm)
		ammonia	neg (5 ppm)
		hydrogen sulfide	neg (5 ppm)
	ground level, pump area (pump P-5)	Hnu	5-50 ppm[1]
		hydrocarbon	0.5-1.0 mg/ℓ[2]
		benzene	6 ppm[3]
FCCU (#1231)	pump rooms below control room	Hnu	2-7 ppm[1]
	2nd level near catalyst and hot oil mixing area	Hnu	3-5 ppm[1]
	compressor room	hydrogen sulfide	15-20 ppm[4]
		mercaptans or other sulfur compounds	20-25 ppm
		benzene	2-4 ppm[3]
		CO	40 ppm
	compressor room control room	Hnu	7-8 ppm[1]
Platformer (#1332)	pump area (P-400A)	Hnu	10-13 ppm[1]
	pump area	Hnu	up to 30 ppm[1]
	other areas	Hnu	<2 ppm[1]
Gulfiner	control room	Hnu	0.8 ppm[1]
	other areas	Hnu	<2 ppm[1]
Sulfur recovery	all over unit	Hnu	<1 ppm[1]

[1]Calibrated with benzene.
[2]As kerosene.
[3]Possible cross-sensitivity to toluene, xylene, and other petroleum hydrocarbons.
[4]Possible interference from SO_2 and other sulfide compounds.

decision was made later in the project to analyze only those samples collected in the FCCU (one of the three selected study process units for Phases II-IV). Table III-2 presents the sampling information and results for the three long-term samples collected at the FCCU. The charcoal tube samples were qualitatively screened for organic compounds using gas chromatography/mass spectrometry. The computer library contains approximately 25,000 compounds. The silica gel tube was analyzed for four aromatic amines: N,N-dimethylaniline, aniline, o-anisidine, and p-anisidine.

The primary emphasis during these Phase I surveys was to collect information through observation and interaction with key personnel. The sampling data generated during 1 day were limited and used only to further familiarize the team with all aspects of refineries. The overall information accumulated during Phase I did allow Enviro to develop a specific study plan which reduced the refinery to three key types of process units, the FCCU, delayed coker unit, and asphalt processing unit.

TABLE III-2. Results of Long-term Area Sampling at FCCU No. 1231

LOCATION	SAMPLE TYPE	SAMPLE DURATION	FLOW RATE	SAMPLE VOLUME	RESULTS
Compressor Room	3 large charcoal tubes in series	246 min	2 ℓ/min	492 ℓ	10 compounds identified as present: 2-Hexene, 3,4,4-Trimethyl- Benzene, 1,3 -Bimethyl- Ethylbenzene Benzene, 1-Ethyl-2-Methyl Benzene, 1,2,3-Trimethyl- Hexane, 3,3 -Dimethyl- Benzene, 1,2-Diethyl Benzene, 1-Methyl-2-(2-Propenyl)- 1-H Idene, 2,3 -Dihydro-1,6-Dimethyl- 1-Heptanol, 2-Propyl-
	silica gel	255 min	200 ml/min	510 ℓ	no aromatic amines detectable
Compressor Room Control Room	3 large charcoal tubes in series	251 min	2 ℓ/min	502 ℓ	no compounds identified as present

IV. STUDY PROCESS UNITS

Three process units were studied at this Gulf refinery, two FCCUs and one deasphalting unit. All three were surveyed in Phase II; in Phase III, one of the FCCUs was not in operation due to a turnaround.

FCCUs - UNITS NO. 1231 AND NO. 1232

A. Unit and Process Description

The two FCCUs are located about 200 yards apart in the northern section of the refinery (Figure II-1). A Claus-type sulfur recovery unit and an HF alkylation unit are located nearby. Unit No. 1232 is the newer and larger of the two FCCUs; it was built in 1954 and has a capacity of about 60,000 bbl/day. Unit No. 1231 was built in 1944 and has a capacity of about 28,000 bbl/day. Both units have side-by-side reactor/regenerator (R/R) structures, CO boilers, separate control rooms and work crews, and similar operating conditions; and both use a synthetic zeolite catalyst. The primary differences between the units are their age, capacity, and the fact that the older unit (No. 1231) is much more enclosed.

Figure IV-1 illustrates the layout of Unit No. 1232 which occupies an area about 125 x 75 yards. The side-by-side R/R structure is located in the middle of the unit at the north boundary. The fractionator and gas-oil stripper towers are located just south of the reactor; a row of about 20 centrifugal pumps is just to the west of these towers. Several heavy-fraction pumps including the charge, slurry reflux and recycle, and decant oil pumps are among these. The control building and CO boiler are situated farther west, and the electrostatic precipitator is situated across a road north of the CO boiler. An enclosed compressor building and catalyst hoppers are on the east side of the R/R area. The recovery section of the unit which includes the absorber-stripper, lean oil still,

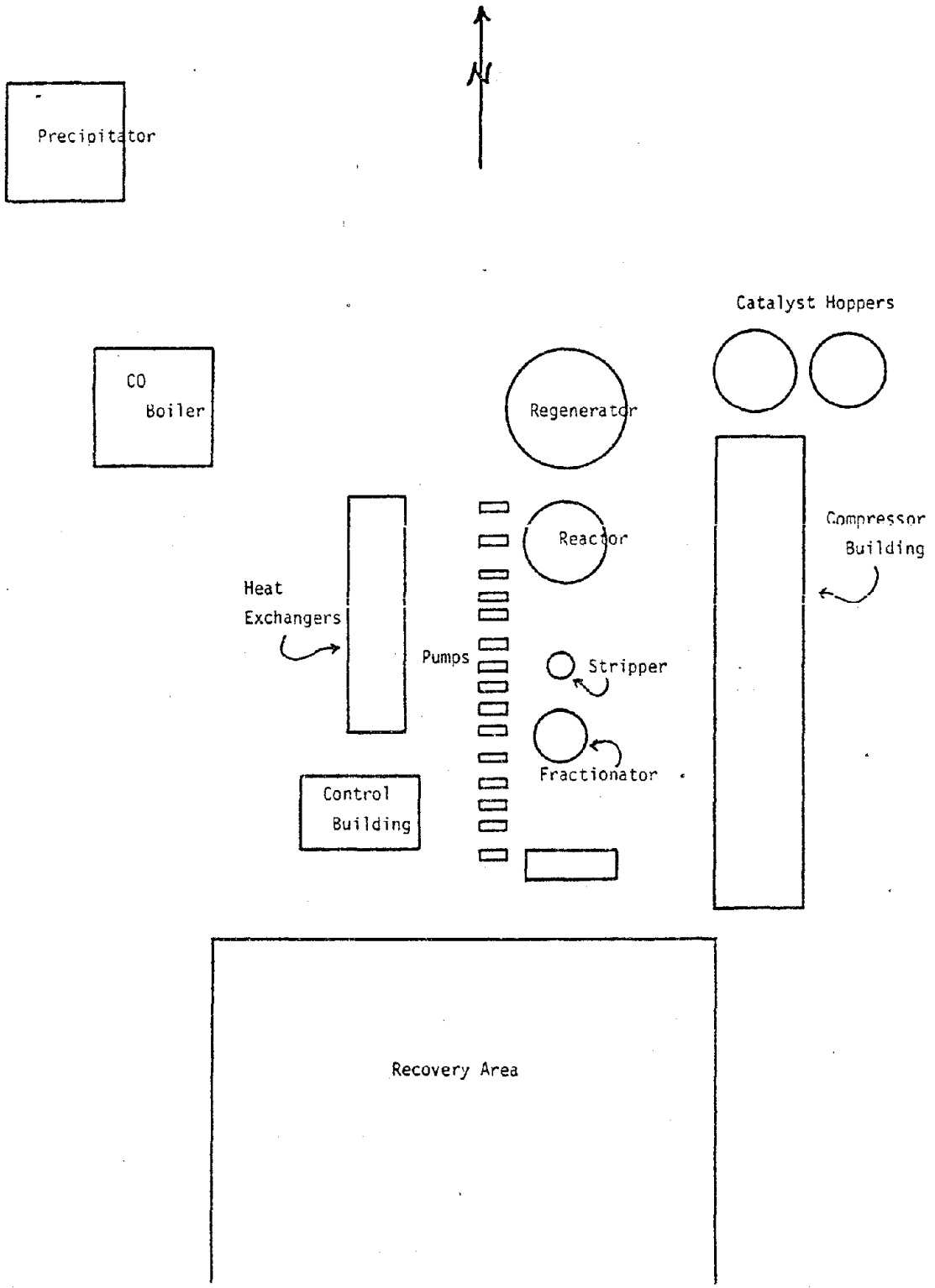


FIGURE IV-1. FCCU No. 1232

debutanizer, depropanizer, and numerous pumps, compressors and heat exchangers occupies a large area south of the control building.

Figure IV-2 illustrates the layout of the main portion of Unit No. 1231 which occupies an area about 100 x 50 yards. A long, narrow, one- and two-story brick building running north and south divides the unit in half. The ground floor of this building is divided into three enclosed pump rooms. The first room (cold pump room) includes the two charge pumps; the second room (hot pump room) includes the slurry recycle, heavy gas oil, and decant oil pumps; and the third room contains the two steam turbine blowers for the spent catalyst leg. The control room is located on the second level of this building above the cold pump room.

The "cat" side of the unit is located west of this main pump building. The side-by-side R/R, fractionator, precipitator, catalyst hoppers, and furnaces are located in this area. The CO boiler (not shown in Figure IV-2) is located farther west of this area across a main refinery road. The recovery side of the unit is located on the east side of the unit and includes two one-story brick buildings. One contains eight large compressors, and the other contains a number of smaller pumps. To the north of these two buildings are the depropanizer, debutanizer, absorber-stripper, and first rerun towers. During the Phase III survey, this Unit No. 1231 was undergoing a major turnaround to eliminate the enclosed pump and compressor buildings.

The basic catalytic cracking process is essentially the same at both FCCUs. Fresh feed consists of atmospheric and vacuum gas oils, and deasphalted gas oils. This feed, preheated by gas-fired charge heaters, plus heavy gas oil and slurry recycle from the fractionator is mixed with the hot catalyst in the two risers at each unit leading to the reactor.

The catalytic cracking takes place in the risers as well as in the reactor. The catalyst used at the Gulf refinery is a synthetic zeolite common to other FCCUs studies in this project. The product vapors and the catalyst are separated (series of cyclones), and the hydrocarbons are taken to the fractionator tower. The catalyst is steam-stripped of any remaining

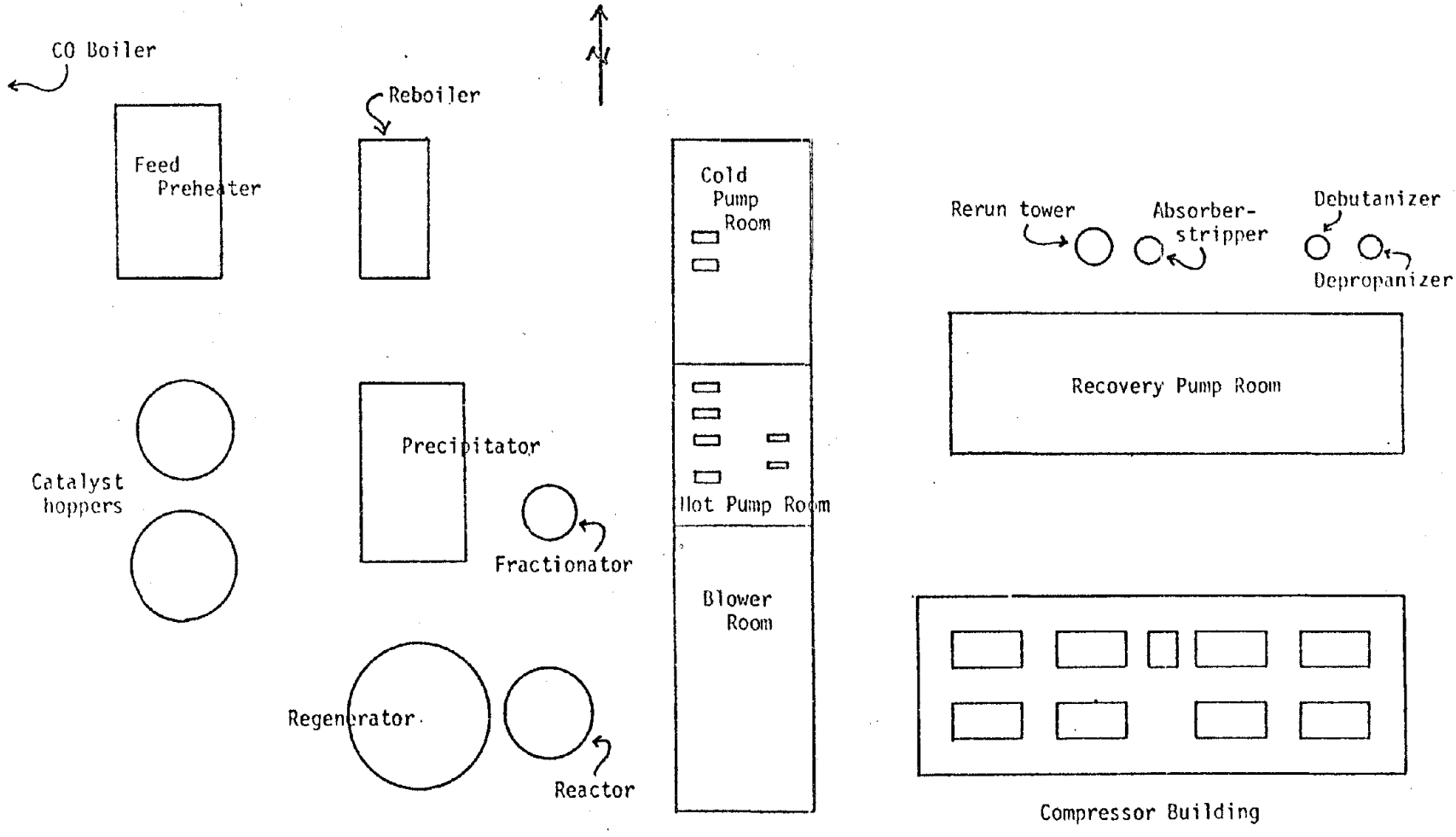


FIGURE IV-2. FCCU No. 1231

oil and delivered to the regenerator through the "spent catalyst leg." In the regenerator, the catalyst is reactivated by oxidizing the accumulated carbon at about 1250°F (677°C). The flue gas from the regenerator goes through a steam generator, through an electrostatic precipitator to remove catalyst fines, and then to the CO boiler where it is burned before being released into the atmosphere. The regenerated catalyst is stripped with steam of any absorbed oxygen before being recirculated back to one of the two risers.

The main products from the fractionator are:

- propane/propene
- butane/butene
- fuel gas
- heavy and light cat gasoline
- heavy and light gas oil

B. Work Force

The work force and job descriptions at both FCCUs are similar. There are normally eight full-time workers per shift at each unit. There are three 8-hour shifts per day, and a total of four work crews rotate to cover the unit 7 days a week. The day shift runs from 0715 to 1515. Each unit is divided into the "cat" side (R/R, fractionator, catalyst hoppers, furnaces) and the "recovery" side for the distribution of job responsibilities. During Phases I and II, there were only seven operators at Unit No. 1231; one operator was handling both sides. Following is a brief description of job activities for the eight full-time workers at Unit No. 1232; however, job titles and description are essentially the same at both units.

- Operator - cat side: Oversees routine operations of the cat side of the unit which includes the R/R, fractionator, heavy-fraction pumps, enclosed compressor building, CO boiler, and precipitator. Normally spends about 50% of his shift outside making visual inspections, supervising and assisting the other operators. When a problem occurs such as a leak or pump failure, he can spend the

majority of his shift outside. Works closely with the control operator and assistant operator to ensure smooth operations of this portion of the unit.

- Assistant operator - cat side: Works for the cat operator; spends about 70% of his shift outside checking pumps, blowers, and other cat side equipment on the ground level as well as above on the various structures. Can perform minor maintenance on equipment.
- Control operator - cat side: Spends about 7½ hours of his shift inside the control room, monitoring and logging in various meters and charts on the cat side of the control board. Once during the day shift, he makes a 30-minute round outside in the cat area, taking about 25 meter and gauge readings.
- Operator - recovery side: Performs the same duties on the recovery side as the cat operator. The recovery side of the unit is located to the south of the cat area. This includes the absorber/stripper, depropanizer, deethanizer, compressors, and pumps.
- Assistant operator - recovery side: General duties similar to those of the cat assistant operator.
- Control operator - recovery side: Duties similar to the other control operator including the daily round.
- Outside control operator: This outside operator, who spends about 70% of his shift in the production area, is not assigned to a particular area of the unit. He can act as a helper wherever he is needed on a particular shift; also has routine duties such as taking quality control samples (mainly evening shift), checking levels, draining and filling various drums, and making periodic rounds of the unit every 2 hours.

- Assistant operator - engineer: Spends about 75% of his shift outside primarily ensuring the smooth running of the pumps, blowers, compressors, and boilers. Performs minor preventive and routine maintenance on these equipment. Spends a good part of his time in and around the enclosed compressor building.

C. Exposure Control Measures

The exposure control measures used at the FCCUs are similar and are typical of those observed at other FCCUs studied during this project. The primary control measure is a closed-system process which limits exposure to products, by-products, and intermediates. Also important is a well-organized maintenance program that provides both efficient preventive and repair maintenance services. Under normal operating conditions, exposure to PAHs may occur from fugitive emissions (especially from pumps), from the regenerator flue gas, during sampling of the various streams, and during maintenance and housekeeping activities.

The fact that the heavy-fraction pumps for Unit No. 1231 are in enclosed rooms without mechanical ventilation greatly increases the potential for airborne PAH accumulation. Pumps such as those for slurry recycle and decant oil streams have been associated with fugitive PAH emissions in previous surveys. It is especially important at this unit that these pumps be maintained properly and that workers spend as little time as possible in these enclosed rooms. Unit No. 1232 is a much more open unit. Although the heavy-fraction pumps are not in an enclosed room, they are located close together near a series of towers (i.e., R/R structure). This is an area where PAH concentration might also be elevated. Both control rooms are air-conditioned but not under positive pressure. Unit No. 1232's control room is occasionally downwind of the R/R or heavy-fraction pumps, while Unit No. 1231's control room is directly above the cold and hot pump rooms. Again, it should be noted that one of the major objectives of the turnaround being performed on Unit No. 1231 during the Phase III survey was to eliminate the enclosed pump and compressor rooms.

The regenerator flue gas is treated the same way at both units. First it goes to an electrostatic precipitator to remove catalyst fines and then is burned in a CO boiler with an auxiliary fuel. The heat produced here is used to generate steam. The CO boiler removes many hydrocarbons as well as carbon monoxide from the flue gas before the effluent is discharged through a stack into the atmosphere.

Most process stream samples, especially the heavy-fraction samples, are collected during the evening shift (1515-2315). Sample bombs are used only for gas samples; liquid samples are collected primarily by the spigot-and-bottle method with sampling loops that eliminate the flushing of lines. The samples are taken to the laboratory for analysis.

Exposure during routine maintenance is difficult to minimize, especially if it occurs in any of the enclosed buildings in Unit No. 1231. There are concrete floors with effective sewer systems in most of these rooms, simplifying cleanup procedures. Most of the major equipment areas (e.g., around pumps) at Unit No. 1232 also have a concrete foundation with a sewer system. The refinery has its own craft maintenance crews (e.g., pipefitters, electricians) that provide preventive and repair services. Both units also have relatively large normal work crews (eight) that can provide a prompt and effective maintenance program.

Hard hats, safety shoes, and rubber gloves with cotton lining are worn routinely by workers on these units, and eye protection is available. There are no routine operations requiring the use of respirators; however, NIOSH-approved air-purifying and self-contained breathing-air respirators are available.

DEASPHALTING UNIT

A. Unit and Process Description

The deasphalting unit (solvent decarbonizer) and the two crude distillation units are located in the northwest corner of the refinery (Figure II-1). The No. 137 crude unit is directly to the west of the deasphalting unit and

the river is to the north. This deasphalting unit processes the residuals from the vacuum tower (crude units) by solvent extraction to produce gas oil and asphalt. The gas oil is used as FCCU feed, and the asphalt is used to produce No. 6 oil. The capacity of the unit is about 22,000 bbl/day of residual. The unit was down during the Phase I visit and was operating at almost 70% of capacity during the Phase II and Phase III visits.

This unit is spread out over an area of about 250 x 200 feet (Figure IV-3). The two deasphalting towers are located in the southwest corner of the unit with the charge oil drum and the gas oil flash tower to the north. The three oil charge pumps are just to the northeast of the deasphalting towers. The two gas-fired furnaces are in the northwest corner, and the air-conditioned control room is located on the extreme east side of the unit. The asphalt flash tower, stripper and pumps, as well as the solvent accumulators, are just to the west of the control room. A series of cooling fans (fin fans) runs from north to south in the center of the unit.

The residuals from the crude units are received in the charge oil drum. The feed is heated by heat exchangers and diluted with solvent before being fed (oil charge pumps) to the center of the deasphalting towers. Here it comes in contact with the liquid butane/propane (70:30), and the liquid-liquid extraction process takes place. Asphalt is removed from the bottom of the reactors, and the extracted oil (gas oil) and propane are removed from the top. The asphalt from both towers passes through a gas-fired heater and then to a flash drum where most of the propane is removed and recycled back to the solvent accumulator. The asphalt then goes to the steam stripper to remove any remaining propane and is pumped (asphalt product pumps) out of the unit to be cut to No. 6 fuel oil.

The oil-propane phase from the deasphalting towers is sent to the oil flash tower where much of the propane and butane is vaporized and recycled back to the solvent accumulator. The oil from the first stage of this flash tower is sent to the gas-fired heater and returned to the flash tower to allow further solvent removal. The remaining solvent is removed from the oil by steam-stripping in the oil stripper. This gas oil is pumped to storage tanks until needed as FCCU charge.

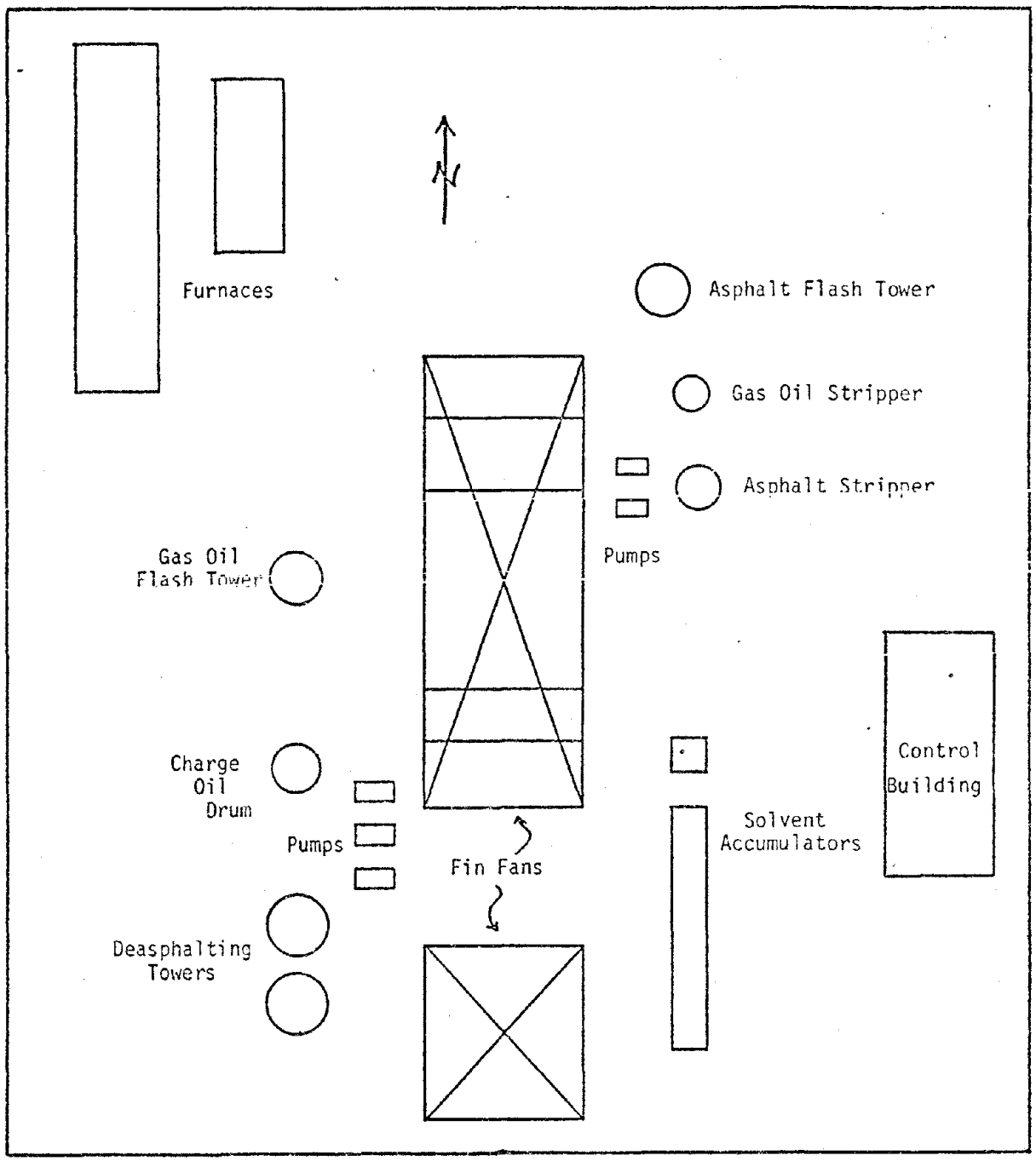


FIGURE IV-3. Deasphalting Unit

B. Work Force

There are three workers assigned full time to the deasphalting unit; shift hours are 0700 to 1900. There are four crews that rotate to cover the 7 days-a-week operation. In addition to these three workers, there is a unit supervisor who has responsibility for this unit and the No. 136 crude unit Monday through Friday from 0700 to 1500. This supervisor normally splits his shift between the control rooms of the two units. Following is a brief description of the duties of the three full-time shift personnel.

- Operator: Supervises overall unit operations. He normally spends about 80-90% of his shift inside where he has responsibility for monitoring and logging in various meters and charts on the control board. He works closely with two assistant operators. He makes periodic inspections of the whole unit and can oversee minor maintenance work.
- Assistant operators (2): These are the two workers who perform the routine outside tasks for this unit; duties are very similar. They normally spend between 50-75% of their shift outside making visual inspections, periodically checking gauges and meters, switching valves, oiling pumps, and performing minor maintenance and general unit housekeeping. They collect a small number of process stream samples (e.g., gas oil, asphalt) during the midnight shift only.

C. Control Measures

As with the two FCCUs, the primary control measure at this deasphalting unit is a closed system. The unit is fairly open without any enclosed production structures or areas encouraging potential vapor accumulation. The only areas of the unit handling heavy fractions with a possibility of PAH

accumulation are around the oil charge pumps and around the asphalt pumps and stripper.

The small control room of this unit is air-conditioned and under positive pressure. An alarm is triggered when the unit is not under positive pressure usually indicating that one of the doors has been left partially open. This is important since the control room is often directly downwind of the asphalt pump area.

The Assistant Operators performed routine cleanup of the unit which is especially important around the asphalt pumps where leaks often occur. The asphalt is cleaned as much as possible with steam. The ground level of the unit is constructed of concrete to simplify cleanup.

V. PHASE II

SAMPLING PROGRAM

A. Protocol

The sampling protocol for Phase II surveys, detailed in the Phase I report (April 1979), was followed as closely as possible during the survey of this Gulf Oil refinery. Since identification of potentially carcinogenic material was the primary objective of this phase (even very small quantities have to be considered significant), area sampling was more appropriate than personal monitoring. Area sampling enabled a larger volume of air to be sampled at selected locations that were considered to be the most likely areas where the compounds would be found, and therefore maximized the chances for identification.

Sampling during this phase was conducted during the day shifts only. A refinery operates in a steady-state mode during the great majority of the time, and during this time, it is expected that the process stream composition within process operations will remain constant. Therefore, for the purpose of this phase, it was assumed that toxic emissions were generally uniform over the three shifts with slight variations due to weather conditions.

B. Sampling Conditions

Weather conditions for the first sampling day (April 11) were partly cloudy skies with the temperatures ranging from 47°F (8°C) in the morning (0900) to 61°F (16°C) by late afternoon (1700). The relative humidity during this time ranged from 29 to 39%. At noon the temperature was 56°F (13°C) with 29% relative humidity, and winds were out of the southwest at 6 mph.

The second sampling day was cloudy with intermittent light rain in the early afternoon becoming heavier in late afternoon. The temperatures ranged from 57°F (14°C) in the morning (0900) to 53°F (12°C) by late afternoon (1700). The relative humidity during this time ranged from 40% at 0900 to 98% at 1700. At noon the temperature was 56°F (13°C) with 67% relative humidity, and winds were out of the west-northwest at 8 mph.

C. Types of Sampling (detailed methods in Phase II report)

The PAHs and azo-heterocyclic compounds were collected using a filter cassette holder containing a silver-membrane filter followed by Chromosorb 102, a porous polymer solid sorbent. High-volume, air-driven Gast pumps and high-flow MSA Model S pumps were used with these cassettes. The critical orifices used with the high-volume pumps were calibrated at about 9.2 ℓ/minute at Enviro prior to the visit; the MSA pumps were calibrated at about 3.0 ℓ/minute using a soapbubble meter. At the refineries, the air-driven pumps were connected to a convenient compressed-air outlet.

The samples were analyzed by gas chromatography/mass spectrometry (GC/MS) in conjunction with high-pressure liquid chromatography (HPLC). This sampling and analytical method allowed quantitative analysis of the following 25 PAH and azo-heterocyclic compounds or groups of compounds:

1. Naphthalene*
2. Quinoline*
3. 2-Methylnaphthalene
4. 1-Methylnaphthalene
5. Acenaphthalene
6. Acenaphthene
7. Fluorene
8. Phenanthrene*/Anthracene*
9. Acridine
10. Carbazole
11. Fluoranthene
12. Pyrene*
13. Benzo(a)fluorene/ Benzo(b)fluorene
14. Benz(a)anthracene*/ Chrysene*/Triphenylene
15. Dimethylbenz(a)-anthracene*

16. Benzo(e)pyrene*/ Benzo(a)pyrene*
17. Perylene
18. Dibenz(a,j)acridine*
19. Dibenz(a,i)carbazole*
20. Dibenzanthracene*
21. Indeno(1,2,3-cd)pyrene*
22. Benzo(g,h,i)perylene
23. Anthanthrene
24. Dibenzpyrene*
25. Coronene

The "*" designates those compounds considered to have some degree of cancer-causing potential (detailed discussion in Phase II report). Although specific isomers of dimethylbenz(a)anthracene, dibenzanthracene and dibenzpyrene are not distinguishable by the analytical method, one or more of their isomers are potential carcinogens; and therefore, the designation is used. There is no definitive information to indicate that the others on this list are potentially carcinogenic. However, the analytical method allowed them to be conveniently included in the analysis, and it was felt that the identification of a large number of PAHs would be beneficial to the study.

Trace metals (Be, As, Cd, Cr, Co, Ni) were sampled for, using a cellulose ester membrane filter in a closed-face cassette. Portable high-flow MSA Model S pumps set at approximately 2 ℓ/minute were used; analysis was performed by atomic absorption.

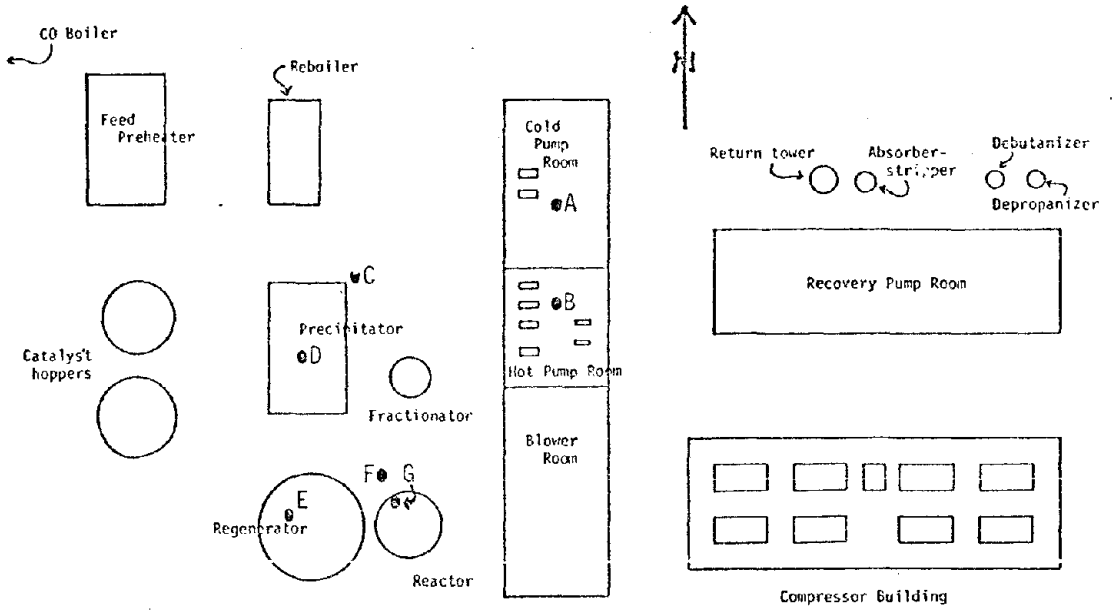
Although aromatic amines are indicated as present in various refinery streams, no information could be found on monitoring data, nor was mention of specific compounds found. Because of this, Enviro attempted in Phase II to identify specific aromatic amines. A limiting factor here was that only seven aromatic amines have established NIOSH sampling and analytical methods. These seven compounds are: aniline, N,N-dimethylaniline, o-toluidine, 2,4-xylidine, o- and p-anisidine, and p-nitroaniline. It was decided that sampling for these seven specific aromatic amines (even though o-toluidine is the only one considered to have some degree of cancer-causing potential) would give a good indication of the presence of this class of compounds. Aromatic amines were collected on large (850-mg) silica gel tubes. High-flow MSA Model S sampling pumps were calibrated at 1 ℓ/minute. Analysis was performed by gas chromatography.

A bubbler containing an alcohol-iodine solution was used for collecting nickel carbonyl. A high-flow MSA Model S sampling pump was calibrated at 2 ℓ/minute. Analysis was performed by atomic absorption.

A method recently developed by the Thermo Electron Company (Waltham, Massachusetts) was used to sample for nitrosamine compounds. The sample was collected on a solid sorbent (proprietary) using a high-flow MSA Model S sampling pump set at 2 ℓ/minute, desorbed with solvent, and analyzed by gas chromatography with a Thermal Energy Analyzer.

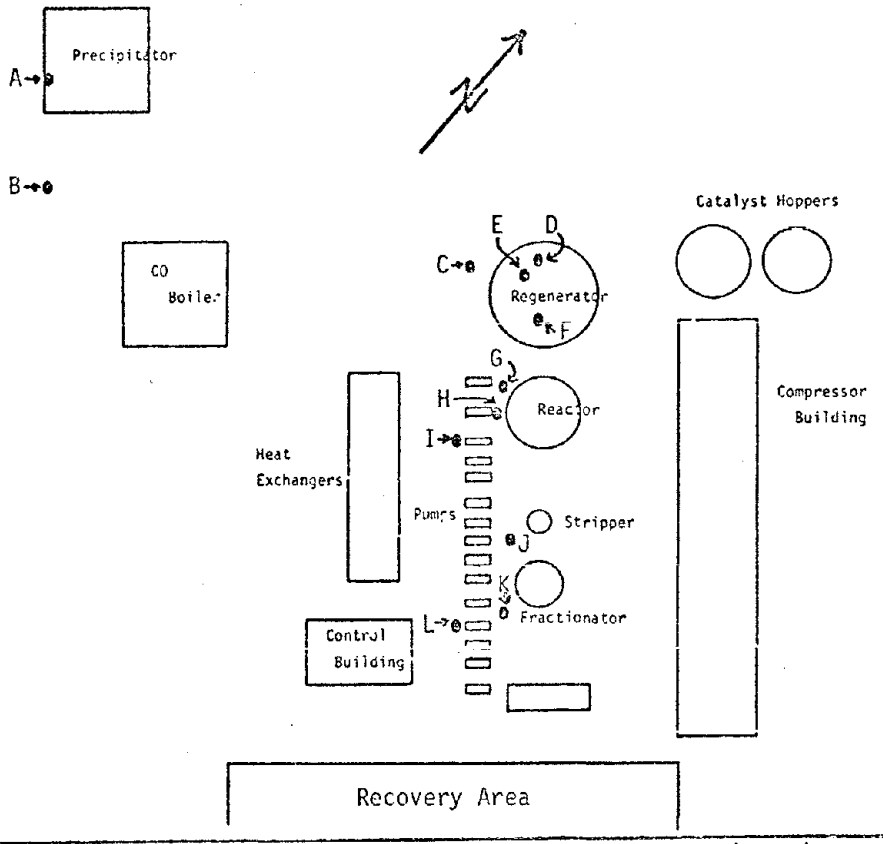
D. Sampling Locations

Figures V-1 through V-3 illustrate the various area sampling locations and sample types at the two FCCUs and deasphalting unit. A single unit upwind sample was collected west of FCCU No. 1231 during both sampling shifts. A refinery upwind sample was collected on the river fence at the northwest corner of the refinery on April 12.



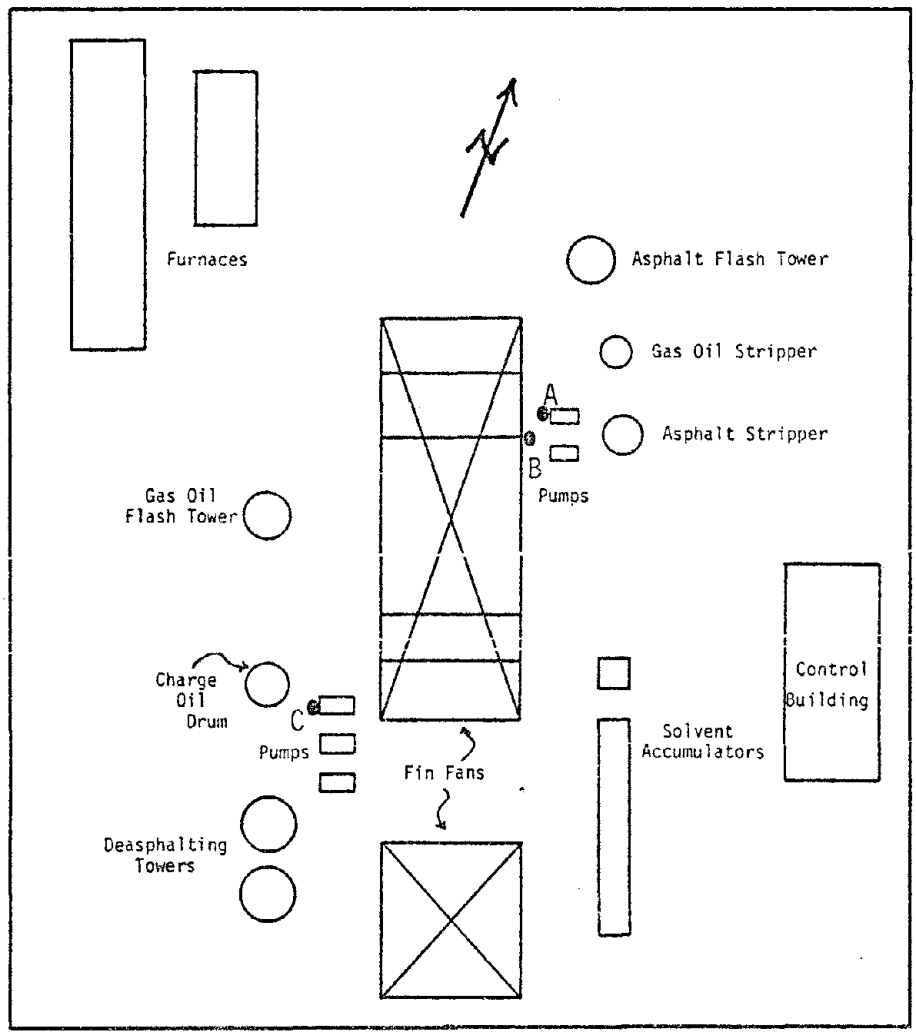
LOCATION	SAMPLE NUMBER	SAMPLE TYPE	DATE
A. Cold pump room near charge and fractionator liquid pumps	202	PAHs	4/11
	205	Aromatic Amines	4/11
B. Hot pump room near slurry and light gas oil pumps	201	PAHs	4/11
	203	Aromatic Amines	4/11
	204	Nitrosamines	4/11
C. Third level above ground, north side of precipitator	214	Trace Metals	4/11
	215	Nickel Carbonyl	4/11
D. Ground level, adjacent to spent catalyst bin	216	Trace Metals	4/11
E. First level up, between riser and catalyst line	212	PAHs	4/11
	213	Aromatic Amines	4/11
F. Ground level, north side of riser at base of stairs	206	PAHs	4/11
	208	Aromatic Amines	4/11
	209	Trace Metals	4/11
	210	Nickel Carbonyl	4/11
	211	Nitrosamines	4/11
G. First level up, north side of riser	207	PAHs	4/11

FIGURE V-1. FCCU No. 1231 Sampling Locations — Phase II



LOCATION	SAMPLE NUMBER	SAMPLE TYPE	DATE
A. Beneath precipitator	239	Trace Metals	4/12
B. South of precipitator, northwest of CO boiler	229	Trace Metals	4/12
C. Beneath steam generator, next to flue gas line	222	PAHs	4/12
D. Six feet from where hot catalyst and charge mix	228	Aromatic Amines	4/12
E. Beneath regenerator	223	PAHs	4/12
F. Beneath riser and regenerator	231 231F	Nickel Carbonyl Trace Metals	4/12 4/12
G. Near charge pumps	220	Aromatic Amines	4/12
H. Near charge pumps	218	PAHs	4/11
I. Near trap-tray reflux pump	226 227	PAHs Aromatic Amines	4/12 4/12
J. Beneath fractionator, near heavy gas oil pump	232	Nickel Carbonyl	4/12
K. Near slurry reflux and recycle pumps	221	Aromatic Amines	4/11
L. Near slurry recycle pump	224 233	PAHs Nitrosamines	4/12 4/12

FIGURE V-2. FCCU No. 1232 Sampling Locations — Phase II



LOCATION	SAMPLE NUMBER	SAMPLE TYPE	DATE
A. On north side of two asphalt pumps	234 235	PAHs Aromatic Amines	4/12 4/12
B. Between asphalt pumps, 10 yards from asphalt stripper	225 236	PAHs Aromatic Amines	4/12 4/12
C. North charge pump, near charge oil drum	237	Aromatic Amines	4/12

FIGURE V-3. Deasphalting Unit Sampling Locations — Phase II

RESULTS AND DISCUSSION

Analytical results of the area air samples collected at this Gulf Oil refinery during Phase II revealed no detectable quantities of the seven nitrosamines, the six trace metals, or nickel carbonyl in any of the samples. Only two of the 12 aromatic amine samples, one from each of the FCCUs, showed any positive results. These two samples showed detectable quantities of one and three aromatic amines, respectively, and each at a concentration less than 0.1 ppm. The results of the PAH samples collected at the FCCUs showed that all samples collected near heavy-fraction pumps had cumulative PAH concentrations considerably higher than those found in the upwind samples. Most of these pump samples had at least eight PAHs identified. The other FCCU samples collected near the R/R structure showed cumulative PAH concentrations comparable to or only slightly higher than the upwind samples. The results of PAH samples collected at the deasphalting unit were also only slightly higher than those of the upwind samples. Following is a more detailed presentation of the Phase II sampling results.

PAHs

Table V-1 shows the complete results of the PAH samples. The upwind unit sample collected west of FCCU No. 1231, but in the midst of the refinery, showed a cumulative PAH concentration of 2.3 $\mu g/m^3$ with three 2-ring PAHs identified. The refinery upwind sample collected at the boundary line yielded a cumulative PAH concentration of only 0.5 $\mu g/m^3$ (4 PAHs identified).

The five samples collected at FCCU No. 1231 had a mean arithmetic cumulative PAH concentration of 100.1 $\mu g/m^3$ with 4 to 11 individual PAHs identified. The sample collected in the hot pump room near the slurry recycle pumps had by far the highest cumulative PAH concentration (466.2 $\mu g/m^3$) of the samples collected at this unit and of all the samples collected at this refinery. Eleven individual PAHs were identified. The sample collected in the cold pump room near the charge pumps yielded a cumulative PAH concentration of 28.3 $\mu g/m^3$ with 10 PAHs identified. The other three samples collected on the ground and first level near the R/R structure

TABLE V-1. Results of PAH Area Samples ($\mu g/m^3$)[a]

		FCCU No. 1231					FCCU No. 1232					D.A.[b]		UPWIND	
Sample Number:		202	202	206	207	212	218	222	223	224	226	225	234	217	238
Sample Volume (m^3):		4.1	4.1	4.0	4.0	2.7	3.6	3.9	3.9	1.8	1.1	2.7	3.7	2.6	3.5
Naphthalene*	(2)[c]	268.00	9.02	0.06	0.70	0.94	21.77	1.35	4.58	17.56	18.86	3.72	0.77	1.17	0.32
Quinoline*	(2)	--[d]	--	--	--	--	3.59	--	--	3.89	5.97	--	--	--	--
2-Methylnaphthalene	(2)	81.71	10.71	0.80	0.93	0.85	28.16	1.30	2.42	42.86	46.91	0.79	0.29	0.72	0.14
1-Methylnaphthalene	(2)	68.35	6.55	0.40	0.47	0.43	13.71	0.54	1.03	25.77	23.24	0.36	0.16	0.36	0.07
Acenaphthalene	(2)	0.34	--	--	--	--	0.12	--	--	--	--	--	--	--	--
Acenaphthene	(2)	5.47	0.21	--	--	--	0.12	--	--	1.02	--	--	--	--	--
Fluorene	(3)	11.67	0.60	--	--	--	0.04	--	--	3.59	--	--	--	--	--
Phenanthrene*/Anthracene*	(3)	23.46	0.89	0.12	0.16	0.04	0.27	--	0.11	17.32	0.10	0.06	0.04	--	0.01
Acridine	(3)	3.61	0.26	--	--	--	--	--	--	0.60	--	--	--	--	--
Carbazole	(3)	0.76	0.05	--	--	--	--	--	--	0.58	--	--	--	--	--
Fluoranthene	(4)	0.65	<0.01	--	--	--	--	--	--	0.23	--	--	--	--	--
Pyrene*	(4)	2.13	0.03	--	--	--	--	--	--	0.09	--	--	--	--	--
Benzo(a)fluorene/ Benzo(b)fluorene	(4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Benz(a)anthracene*/ Chrysene*/Triphenylene	(4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Dimethylbenz(a)anthracene*	(4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(e)pyrene*/ Benzo(a)pyrene*	(5)	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Perylene	(5)	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,j)acridine*	(5)	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,i)carbazole*	(5)	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Dibenzanthracene*	(5)	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Indeno(1,2,3-cd)pyrene*	(6)	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(g,h,i)perylene	(6)	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Anthanthrene	(6)	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Dibenzopyrene*	(6)	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Coronene	(7)	--	--	--	--	--	--	--	--	--	--	--	--	--	--
TOTAL		466.15	28.33	1.38	2.26	2.26	67.78	3.19	8.19	113.51	95.08	4.93	1.26	2.25	0.54

* Suggested as having some cancer-causing potential.
[a] Blank values have been subtracted out of data.
[b] D.A. = deasphalting unit.
[c] ( ) = ring number.
[d] "--" designates none detected.

showed a mean cumulative PAH concentration of only 2.0 $\mu g/m^3$ with each sample having four PAHs identified. Almost all PAHs identified at this unit were the lighter molecular weight, 2-ring (91.1%) and 3-ring (8.3%) compounds.

The five samples collected at FCCU No. 1232 had a mean cumulative PAH concentration of 56.6 $\mu g/m^3$ with 3 to 11 individual PAHs identified. The three samples collected near pumps were again much higher (mean cumulative PAH concentration of 92.1 $\mu g/m^3$) than the two collected near the R/R structure (5.7 $\mu g/m^3$), and as before almost all of the PAHs identified were 2-ring (92.2%) and 3-ring (7.7%) compounds.

The two samples collected at the deasphalting unit (near the heavy-fraction pumps) had a mean cumulative concentration of only 3.1 $\mu g/m^3$; both had four PAHs identified. Almost all of the PAHs found were 2-ring compounds (98.4%), with the rest being 3-ring compounds (1.6%)

Aromatic Amines

Table V-2 shows the results of aromatic amine samples. Of the 12 silica gel samples analyzed, only two had detectable quantities of any of the seven aromatic amines. One of these samples, collected in the hot pump room of FCCU No. 1231, showed air concentrations of 0.05 ppm aniline, 0.02 ppm o-anisidine, and 0.08 ppm p-anisidine as time-weighted averages over the sampling period. The other positive sample was collected in the pump area at FCCU No. 1232 and showed an air concentration of 0.06 ppm p-anisidine.

In addition to the seven aromatic amines for which the sampling and analytical method is NIOSH-validated, the silica gel samples were also analyzed for 1-naphthylamine by the same method. This aromatic amine is strongly suspected of being carcinogenic but not specifically associated with refinery operations. None of the 12 samples analyzed had detectable quantities of this compound.

TABLE V-2. Results of Aromatic Amine Area Samples (ppm)

SAMPLE NUMBER	PROCESS UNIT	SAMPLE VOLUME (m^3)	ANILINE	N,N-DIMETHYL ANILINE	O-TOLUIDINE	2,4-DIMETHYL ANININE	O-ANSIDINE	P-ANISIDINE	1-NAPHTHYLAMINE	P-NITROANILINE
203	FCCU 1231	0.481	<.05	<.05	<.05	<.05	<.01	*0.06	<.05	<.05
205	FCCU 1231	0.614	<.05	<.05	<.05	<.05	<.01	<.01	<.05	<.05
208	FCCU 1231	0.541	<.05	<.05	<.05	<.05	<.01	<.01	<.05	<.05
213	FCCU 1231	0.515	<.05	<.05	<.05	<.05	<.01	<.01	<.05	<.05
220	FCCU 1232	0.421	<.05	<.05	<.05	<.05	<.01	<.01	<.05	<.05
221	FCCU 1232	0.410	<.05	<.05	<.05	<.05	<.01	<.01	<.05	<.05
227	FCCU 1232	0.457	*0.05	<.05	<.05	<.05	*0.02	*0.08	<.05	<.05
228	FCCU 1232	0.492	<.05	<.05	<.05	<.05	<.01	<.01	<.05	<.05
235	D.A.†	0.459	<.05	<.05	<.05	<.05	<.01	<.01	<.05	<.05
236	D.A.	0.438	<.05	<.05	<.05	<.05	<.01	<.01	<.05	<.05
237	D.A.	0.400	<.05	<.05	<.05	<.05	<.01	<.01	<.05	<.05

* Indicates compound actually identified; all other values express the detection limit of the compound of interest.

† D.A. = deasphalting unit.

Trace Metals

Table V-3 shows the results of the trace metal analysis. There were no detectable quantities of any of the six metals (Co, Cr, Ni, Cd, As, Be) in any of the six area samples analyzed (three from each FCCU). It should be noted that metal catalysts were not used in the FCCUs.

TABLE V-3. Results of Trace Metal Area Samples ($\mu g/m^3$)*

SAMPLE NUMBER	UNIT PROCESS	SAMPLE VOLUME (m^3)	Co	Cr	Ni	Cd	As	Be
209	FCCU 1231	0.930	<3.2	<3.8	<3.8	<0.3	<0.1	<0.1
214	FCCU 1231	0.888	<3.4	<3.4	<3.4	<0.3	<0.1	<0.1
216	FCCU 1231	0.911	<3.3	<3.3	<3.3	<0.3	<0.1	<0.1
229	FCCU 1232	0.909	<3.3	<3.3	<3.3	<0.3	<0.1	<0.1
230	FCCU 1232	0.888	<3.4	<3.4	<3.4	<0.3	<0.1	<0.1
231F	FCCU 1232	0.812	<3.7	<3.7	<3.7	<0.4	<0.1	<0.1

* All six metals were not detected in any of the six (6) samples; values express detection limits.

Nickel Carbonyl

Table V-4 shows the results of the nickel carbonyl analysis. Nickel carbonyl was not detectable in any of the four area samples analyzed (two from each FCCU). The minimum detectable concentrations for these samples ranges from 1.7 to 3.1 $\mu g/m^3$ depending on the sample volume.

TABLE V-4. Results of Nickel Carbonyl Area Samples ($\mu g/m^3$)*

SAMPLE NUMBER	UNIT PROCESS	SAMPLE VOLUME (m^3)	$Ni(CO)_4$
210	FCCU 1231	0.866	<1.7
215	FCCU 1231	0.523	<2.9
231	FCCU 1232	0.629	<1.8
232	FCCU 1232	0.491	<3.1

* Nickel carbonyl not detected in any of the four (4) samples; values express detection limit.

Nitrosamines

Table V-5 shows the results of the nitrosamine area samples. There were no detectable quantities of any of the seven nitrosamines in the three area samples analyzed (two from FCCU No. 1231, one from FCCU No. 1232). The lower limit of detection was 3.7-5.9 $\mu g/m^3$ of air for each nitrosamine depending on the sample volume.

TABLE V-5. Results of Nitrosamine Area Samples ($\mu g/m^3$)*

SAMPLE NUMBER	UNIT PROCESS	SAMPLE VOLUME (m^3)	NDMA	NDEA	NDPA	NDBA	NPYR	NMOR	NPIP
204	FCCU 1231	1.080	<3.7	<3.7	<3.7	<3.7	<3.7	<3.7	<3.7
211	FCCU 1231	0.805	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
233	FCCU 1232	0.673	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9	<5.9

NDMA:N-nitrosodimethylamine
NDEA:N-nitrosodiethylamine
NDPA:N-nitrosodiproplyamine
NDBA:N-nitrodibutylamine
NPIP:N-nitrosopiperidine
NPYR:N-nitrosopyrrolidine
NMOR:N-nitrosomorpholine

* All seven nitrosomaines were not detected in any of the three (3) samples; values express detection limits.

VI. PHASE III

SAMPLING PROGRAM

A. Protocol

The sampling protocol for Phase III surveys, detailed in the Phase II report (November, 1979), was followed as closely as possible during the survey of this Gulf Oil refinery. Sampling for airborne PAHs was conducted during the day shifts on the second and third days of the survey in the two study process units. As mentioned previously, FCCU No. 1231 was not in operation during this survey. Because of this, personal as well as area samples were collected in the deasphalting unit which had originally been scheduled for area sampling only. Two locations were chosen in each unit where area samples were collected. The area sampling cassette containing a silver-membrane filter followed by Chromosorb 102 (Figure VI-1) was used with a portable MSA Model S pump calibrated at 2.0 ℓ/minute. To investigate the size distribution of airborne particles in the study process units, a total particulate area air sample was collected at each sampling site for optical sizing. These samples were collected using an open-face cassette containing a mixed cellulose ester filter (0.45-μm pore size) and a portable MSA Model S pump calibrated at 2.0 ℓ/minute. A modified sampling device (Figure VI-2) was used for personal monitoring for PAHs. The Chromosorb 102 was packed in a glass tube following the cassette rather than in the cassette itself. An upwind sample was collected each sampling day; the first day at the south side of the refinery near wharf 3, and the second day at the northwest corner near crude unit 137. A total of 27 samples was collected over the 2 days.

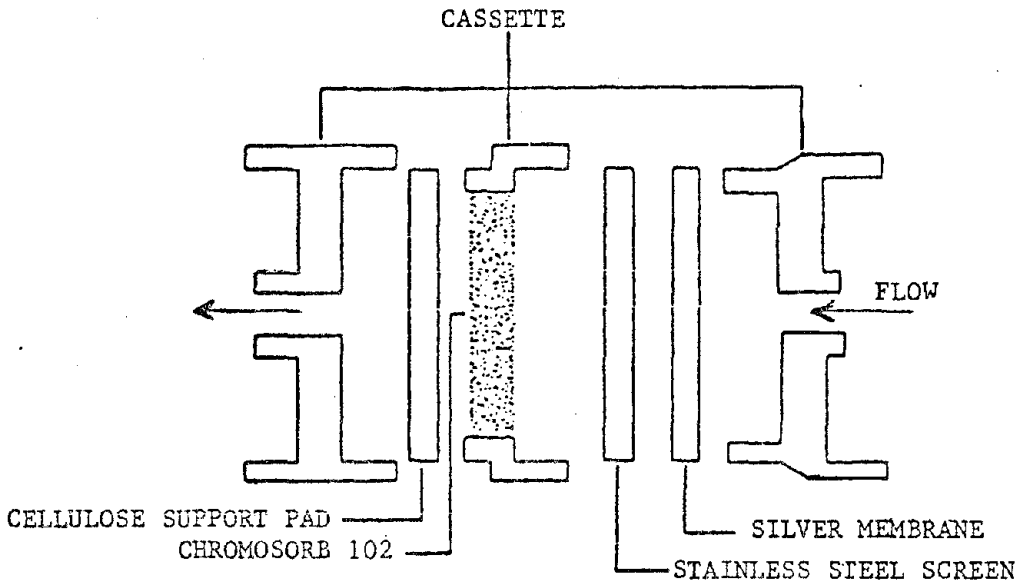


FIGURE VI-1. Area Monitoring Device for PAHs

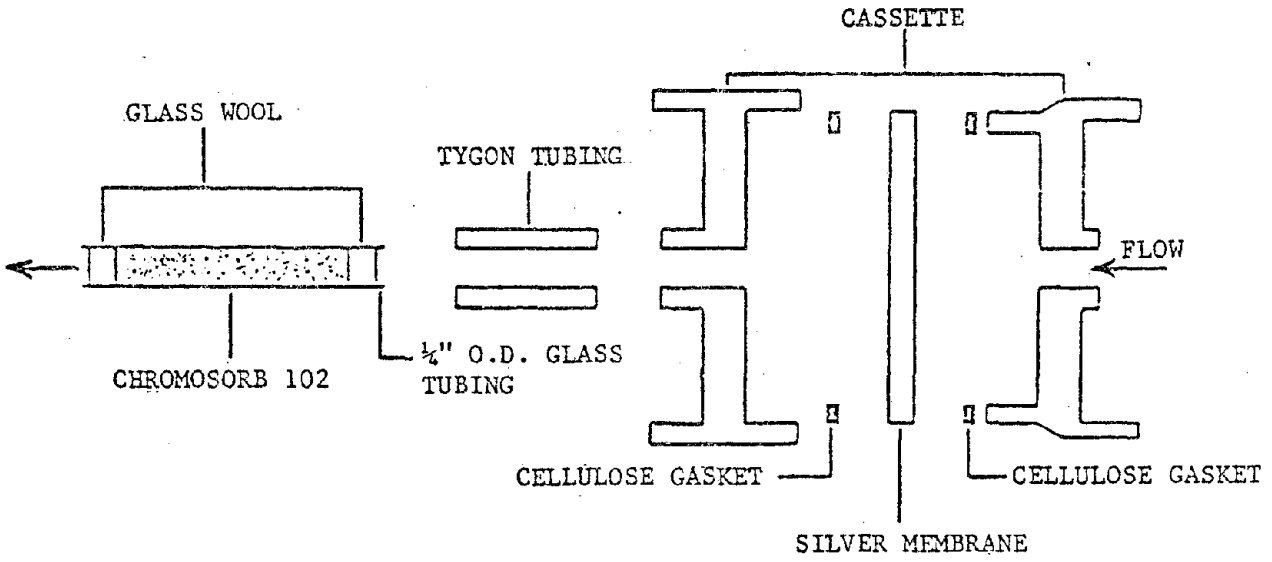


FIGURE VI-2. Personal Monitoring Device for PAHs

The analytical method for PAHs used in Phase III was a modification of the method used in Phase II. Gas chromatography/mass spectrometry was again used but without high-pressure liquid chromatography that is needed to resolve some of the groups of PAHs. This difference reduced the number of individual or groups of PAHs, for which the method is capable of analyzing, from 25 to the 23 listed below.

1. Naphthalene*
2. Quinoline*
3. 2-Methylnaphthalene
4. 1-Methylnaphthalene
5. Acenaphthalene
6. Acenaphthene
7. Fluorene
8. Phenanthrene*/Anthracene*
9. Acridine
10. Carbazole
11. Fluoranthene
12. Pyrene*
13. Benzofluorene
14. Benz(a)anthracene*/ Chrysene*/Triphenylene
15. Benzo(e)pyrene*/ Benzo(a)pyrene*
16. Perylene
17. Dibenz(a,j)acridine*
18. Dibenz(a,i)carbazole*
19. Ideno(1,2,3-cd)pyrene*
20. Dibenzanthracene*
21. Benzo(g,h,i)perylene
22. Coronene
23. Dibenzpyrene*

The "*" designates those compounds considered to have some degree of cancer-causing potential (detailed discussion in Phase II report). As with the Phase II method, the specific isomers of dibenzanthracene and dibenzpyrene are not distinguishable.

For sizing, the particulate sample is prepared for optical microscopy by rendering the mixed ester filter transparent with an immersion fluid. The prepared slide is focused in the field of the optical microscope, and particles are sized using a Porton reticle grid, which is mounted in the ocular lens so that the grid is superimposed on the field of the microscope. The reticle is calibrated at the magnification to be used by means of a stage micrometer.

B. Sampling Conditions

Weather conditions for the first sampling day (April 2) were sunny with partly cloudy skies; the temperature ranged from 45°F (7°C) in the morning (0700) to about 70°F (21°C) by early afternoon (1400). The relative humidity during this period ranged from 80% to 40% with the winds from the south at 3-12 mph.

Skies were sunny and clear on April 3, with the temperature ranging from 45°F (7°C) at 0700 to 70°F (21°C) by 1400. Relative humidity ranged from 80% to 35% with winds from the northwest at 0-10 mph.

C. FCCU No. 1232

Air Sampling

Two locations in the pump area near the R/R structure and the fractionator (Figure VI-3) were selected to collect the area samples at FCCU No. 1232. Location F-1, 3 feet above one of the charge pumps at the north end of the row of pumps, was sampled on April 2 during the day shift. Location F-2, above a slurry recycle pump and near other heavy-fraction pumps, was sampled on April 3. The slurry recycle pump (steam-driven centrifugal pump) returns the fractionator tower bottoms, which include spent catalyst, back to the reactor.

Personal Sampling

All eight FCCU shift workers described in Chapter IV were sampled during the day shifts on April 2 and 3.

D. Deasphalting Unit

Area Sampling

Figure VI-4 shows the two area sampling sites selected at the deasphalting unit. Location D-1, 4 feet above ground on the middle charge pump and near the charge oil drum, was sampled on April 2.

Location D-2 was about 2 feet above the south asphalt pump near the asphalt stripper. This location was sampled on April 3.

Personal Sampling

The three shift workers described in Chapter IV were sampled during the day shifts on both sampling days.

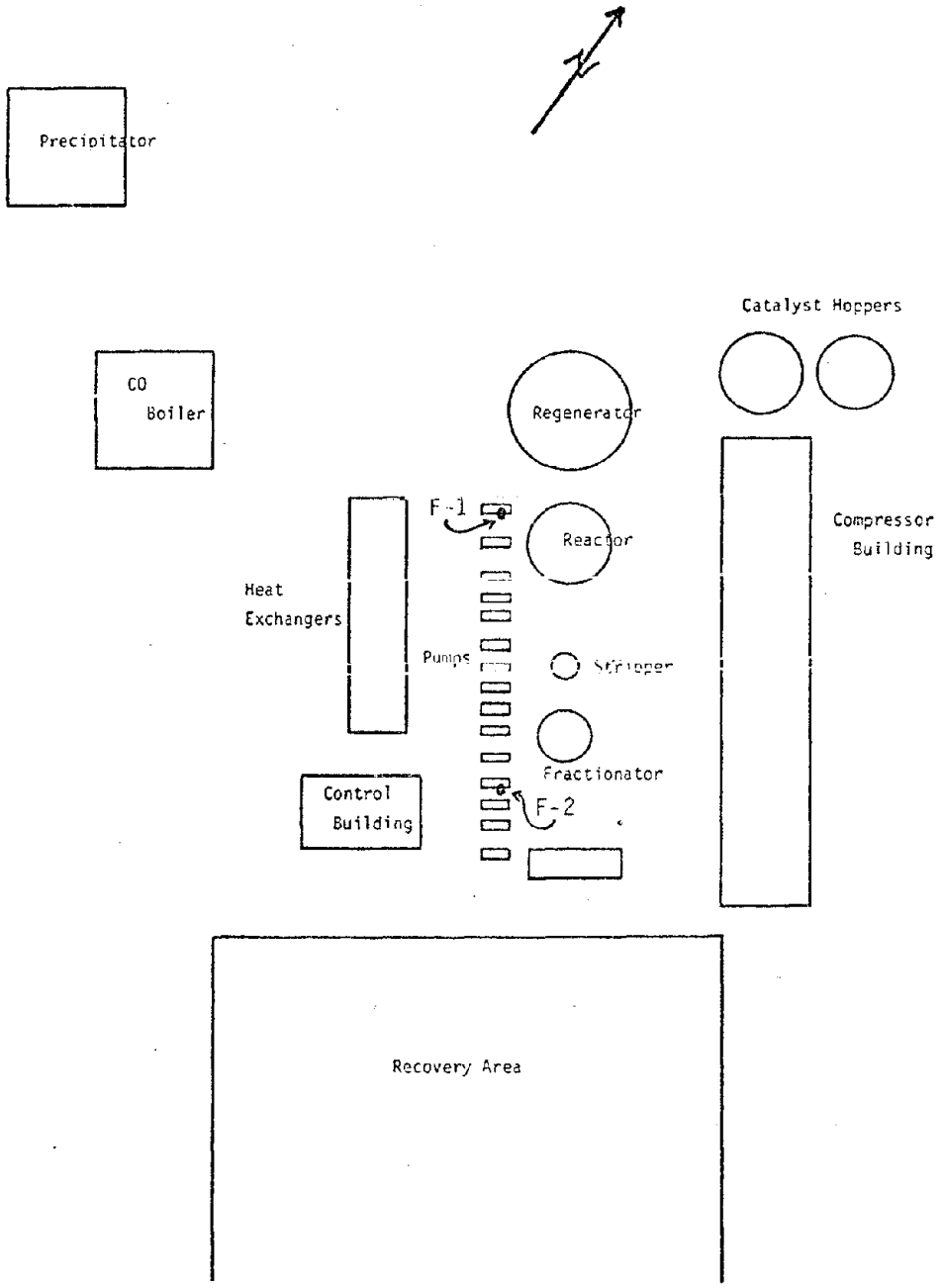


FIGURE VI-3. FCCU No. 1232 Sampling Locations - Phase III

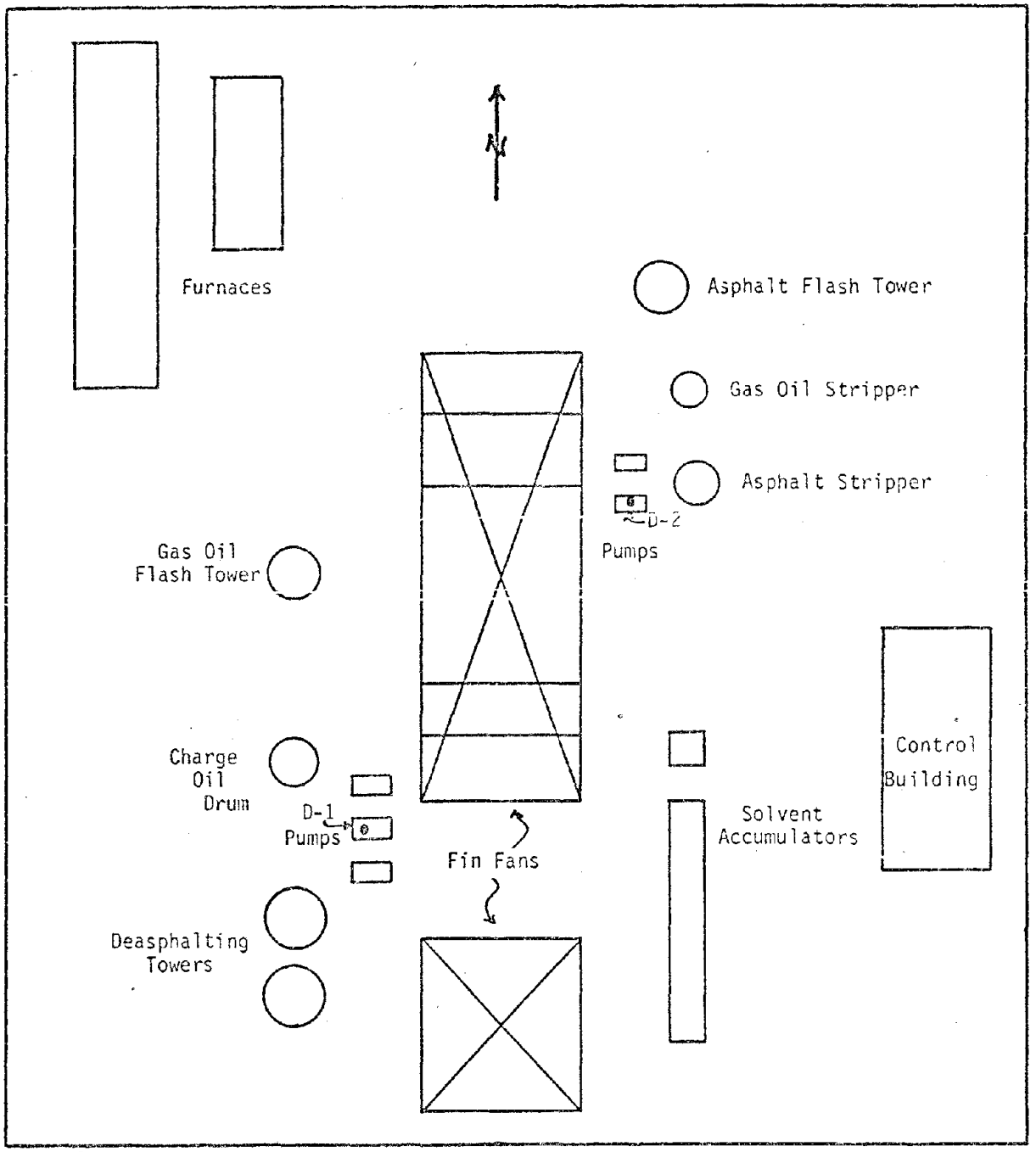


FIGURE VI-4. Deasphalting Unit Sampling Locations - Phase III

RESULTS AND DISCUSSION

The complete results of the area and personal PAH samples collected at this Gulf Oil refinery are presented in Tables VI-1 and VI-2. All 25 personal and area air samples analyzed from the two study process units had detectable quantities of at least four of the 23 PAHs (or groups of PAHs) for which the samples were analyzed. The cumulative PAH concentrations for individual samples ranged from 2.0 $\mu g/m^3$ for a personal sample collected from one of the FCCU operators to as high as 202.2 $\mu g/m^3$ for an FCCU area sample. The upwind boundary samples were both less than 1 $\mu g/m^3$.

A summary of the personal and area sampling results, including the mean (arithmetic) cumulative PAH concentrations ($\bar{X}$) for the two units, is presented in Table VI-3. On the average, personal samples at the deasphalting unit were greater than those from the FCCU; however, the average number of PAHs identified in the FCCU personal samples was greater than that for the deasphalting unit (7.6 versus 5.6 PAHs). The FCCU showed a much higher mean cumulative PAH concentration for the area samples; this was due to one of the two FCCU area samples being exceptionally high.

The distribution of individual PAHs by ring number was consistent in all samples. The 2-ring compounds were found by far in the highest concentrations and as the ring number increased the concentration decreased. None of the 6- or 7-ring PAHs were found.

TABLE VI-1. PAH Analytical Results (μg/m³) for Personal and Area Samples Collected at FCCU No. 1232[a]

Ring No.	Sample Location:	AREA		OPERATOR				CONTROL OPERATOR				ASSISTANT OPERATOR				OUTSIDE		ASST. OPER.	
		F-1	F-2	Cat Side		Recov. Side		Cat Side		Recov. Side		Cat Side		Recov. Side		CONT. OPER.		ENGINEER	
	Sample Date:	4/2	4/3	4/2	4/3	4/2	4/3	4/2	4/3	4/2	4/3	4/2	4/3	4/2	4/3	4/2	4/3	4/2	4/3
	Sample Volume (ℓ):	829	791	879	810	873	884	877	827	911	881	874	838	870	885	898	866	880	854
	Sample Time:	0705-1410	0704-1405	0647-1400	0707-1356	0640-1401	0643-1403	0651-1405	0650-1354	0634-1403	0639-1354	0649-1406	0637-1351	0645-1402	0645-1401	0637-1406	0641-1352	0644-1413	0646-1353
(2)	Naphthalene*	1.64	23.38	1.20	6.68	0.85	0.22	0.16	3.01	0.24	5.32	0.89	7.23	--[b]	0.65	0.66	12.89	1.12	3.77
(2)	Quinoline*	0.21	3.28	--	--	--	--	--	0.23	--	0.33	--	0.57	--	--	--	--	0.11	0.06
(2)	2-Methylnaphthalene	5.75	105.93	5.35	9.26	3.75	0.93	2.23	6.12	2.10	5.93	3.63	16.58	0.68	1.10	2.64	28.89	4.07	7.69
(2)	1-Methylnaphthalene	3.29	42.24	3.14	5.85	2.27	0.55	1.46	3.84	1.28	3.49	2.03	10.90	0.44	0.58	1.78	14.53	2.41	4.09
(2)	Acenaphthalene	0.14	2.80	0.18	0.26	0.12	--	0.10	0.29	0.07	0.21	0.11	0.52	0.04	0.03	0.10	--	0.10	0.08
(2)	Acenaphthene	0.29	5.47	0.55	0.64	0.44	0.04	0.40	0.88	0.36	0.61	0.41	1.77	0.27	0.16	0.31	1.17	0.32	0.79
(3)	Fluorene	0.28	3.44	0.24	0.58	0.19	--	0.17	0.35	0.12	0.23	0.16	0.58	0.07	0.03	0.13	0.60	0.08	0.08
(3)	Phenanthrene*/Anthracene*	0.32	10.80	0.67	1.27	0.64	0.21	0.66	1.21	0.43	0.23	0.55	1.60	0.81	0.12	0.15	1.83	0.11	0.75
(3)	Acridine	0.14	1.54	--	--	--	--	<0.01	--	--	0.01	0.03	0.16	--	0.01	--	--	<0.01	--
(3)	Carbazole	0.02	0.53	<0.01	0.02	--	--	--	--	--	--	--	<0.01	--	--	--	--	--	--
(4)	Fluoranthene	0.04	0.58	<0.01	0.03	--	--	<0.01	0.05	--	--	<0.01	0.01	0.06	--	--	0.07	--	--
(4)	Pyrene*	0.04	1.35	<0.01	0.05	--	--	--	0.03	--	--	<0.01	0.04	0.02	<0.01	--	0.13	--	--
(4)	Benzofluorene	--	0.47	--	--	--	--	--	--	--	--	--	--	--	--	--	<0.01	--	--
(4)	Benz(a)anthracene*/ Chrysene*/Triphenylene	--	0.35	--	--	--	--	--	--	--	--	--	--	--	--	--	0.08	--	--
(5)	Benzo(e)pyrene*/ Benzo(a)pyrene*	--	0.01	--	--	--	--	--	--	--	--	--	--	--	--	--	0.02	--	--
(5)	Perylene	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
(5)	Dibenz(a,j)acridine*	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
(5)	Dibenz(a,i)carbazole*	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
(6)	Indeno(1,2,3-cd)pyrene*	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
(5)	Dibenzanthracene*[c]	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
(6)	Benzo(g,h,i)perylene	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
(7)	Coronene	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
(6)	Dibenzpyrene*[c]	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	TOTAL	12.16	202.17	11.33	24.64	8.26	1.95	5.18	16.01	4.60	16.43	7.81	39.96	2.39	2.68	5.77	60.21	8.32	17.31

* Suggested as having some cancer-causing potential.

[a] Blank values have been subtracted from data. Data have not been corrected for temperature and pressure variation; maximum deviation would be within ±2% of actual values.

[b] "--" designates compounds not detected.

[c] Specific isomers not distinguishable by analytical method; reported value represents any one or combination of existing isomers.

TABLE VI-2. PAH Analytical Results (μg/m³) for Personal and Area Samples Collected at the Deasphalting Unit and Upwind Locations[a]

Ring No.	Sample Location:	AREA		OPERATOR		ASSISTANT OPERATOR 1		ASSISTANT OPERATOR 2		UPWIND	
		D-1	D-2								
	Sample Date:	4/2-	4/3	4/2	4/3	4/2	4/3	4/2	4/3	4/2	4/3
	Sample Volume (ℓ):	878	789	879	858	864	836	[b]	838	850	700
	Sample Time:	0738-1440	0735-1424	0721-1436	0718-1427	0723-1437	0731-1429		0731-1422	0758-1459	0623-1213
(2)	Naphthalene*	36.93	24.92	18.13	2.52	42.15	19.69		1.71	--[c]	0.29
(2)	Quinoline	--	0.06	--	<0.01	0.12	--		--	--	<0.01
(2)	2-Methylnaphthalene	2.81	2.31	1.47	0.57	4.67	0.81		0.38	--	0.24
(2)	1-Methylnaphthalene	1.07	1.06	0.81	0.33	2.25	0.40		0.36	--	0.25
(2)	Acenaphthalene	--	0.04	--	--	0.04	--		--	--	--
(2)	Acenaphthene	--	0.11	--	0.02	0.18	--		<0.01	--	--
(3)	Fluorene	--	0.07	--	--	0.09	--		--	--	--
(3)	Phenanthrene*/Anthracene*	0.33	0.10	0.33	--	0.22	0.39		0.05	--	--
(3)	Acridine	--	0.05	--	--	0.03	--		--	--	--
(3)	Carbazole	<0.01	0.01	--	--	--	--		--	--	--
(4)	Fluoranthene	0.01	0.03	--	--	<0.01	--		--	--	--
(4)	Pyrene*	0.01	0.04	--	--	--	--		--	--	--
(4)	Benzofluorene	--	--	--	--	--	--		--	--	--
(4)	Benz(a)anthracene*/ Chrysene*/Triphenylene	--	--	--	--	--	--		--	--	--
(5)	Benzo(e)pyrene*/ Benzo(a)pyrene*	--	--	--	--	--	--		--	--	--
(5)	Perylene	--	--	--	--	--	--		--	--	--
(5)	Dibenz(a,j)acridine*	--	--	--	--	--	--		--	--	--
(5)	Dibenz(a,i)carbazole*	--	--	--	--	--	--		--	--	--
(6)	Indeno(1,2,3-cd)pyrene*	--	--	--	--	--	--		--	--	--
(5)	Dibenzanthracene*[d]	--	--	--	--	--	--		--	--	--
(6)	Benzo(g,h,i)perylene	--	--	--	--	--	--		--	--	--
(7)	Coronene	--	--	--	--	--	--		--	--	--
(6)	Dibenzpyrene*[d]	--	--	--	--	--	--		--	--	--
TOTAL		41.16	28.88	20.74	3.44	49.75	21.29		2.50	0.00	0.79

* Suggested as having some cancer-causing potential.
[a] Blank values have been subtracted from data. Data have not been corrected for temperature and pressure variation; maximum deviation would be within ±2% of actual values.
[b] Sample lost.
[c] "--" designates compounds not detected.
[d] Specific isomers not distinguishable by analytical method; reported value represents any one or combination of existing isomers.

TABLE VI-3. Summary of PAH Results

	PERSONAL SAMPLES			AREA SAMPLES		
	NO. OF SAMPLES	$\bar{X}$(μg/m³)	NO. OF PAHs	NO. OF SAMPLES	$\bar{X}$(μg/m³)	NO. OF PAHs
FCCU No. 1232	16	14.6	5-12	2	107.2	12-15
D.A.[a]	5	19.5	4-10	2	35.0	7-12
TOTAL	21	15.8	4-12	4	71.1	7-15

[a] D.A. - deasphalting unit.

A. FCCU

The mean cumulative PAH concentration over the two shifts for the eight FCCU workers was 14.6 $\mu g/m^3$ with the number of individual PAHs ranging from 5 to 12. Table VI-4 shows the mean cumulative PAH concentration ($\bar{X}$) and numbers of PAHs identified for the operators categorized by work area within the FCCU. The three operators assigned to the cat side (includes the R/R, fractionator, pumps, and compressor building) showed a mean cumulative PAH concentration ($\bar{X}$ = 17.5 $\mu g/m^3$) almost three times greater than that for the three operators assigned to the recovery side ($\bar{X}$ = 6.1 $\mu g/m^3$). The number of PAHs identified were also greater for the cat side operator samples. This was expected due to the nature of the process streams in each of the unit areas. The two operators who work the whole unit showed a mean cumulative PAH concentration of 22.9 $\mu g/m^3$ which is quite similar to the other cat side operators not including the control operator who spends almost 95% of his shift inside. During the two sampling shifts it did appear that these two total-unit operators spent a majority of their outside time in the cat side. The control room, where all the operators spend at least 25% of their shift, is within the cat side of the unit.

TABLE VI-4. Personal Monitoring Results - FCCU No. 1232

	NO. OF SAMPLES	$\bar{X}(\mu g/m^3)$	NO. OF PAHs
Operators - Cat side	6	17.5	9-12
Operator	2	18.0	10
Assistant Operator	2	23.9	10-12
Control Operator (inside)	2	10.6	9-10
Operators - Recovery side	6	6.1	5-9
Operator	2	5.1	5-7
Assistant Operator	2	2.5	8-9
Control Operator (inside)	2	10.5	7-9
Operators - Both sides	4	22.9	7-11
Outside Control Operator	2	33.0	7-11
Assistant Operator - Engineer	2	12.8	8-9
TOTAL	16	14.6	5-12

Table VI-4 also shows that the two inside control operators were exposed at lower cumulative concentrations than the four outside operators who worked the "cat side" and "both sides," and at higher concentrations than the two outside operators who worked the recovery side. This is a further indication that PAH emissions were primarily in the cat area of the unit.

Table VI-1 shows that seven out of the eight personal samples collected on April 3 were higher than the duplicate samples collected on April 2. The mean cumulative PAH concentration for the eight personal samples collected the first day was 6.7 $\mu g/m^3$ compared to 22.5 $\mu g/m^3$ the second sampling day. This difference could not be explained by any environmental or operational conditions during the 2 sampling days. Both day shifts during which sampling was performed were described as routine by the workers. The weather conditions were also fairly similar during the 2 days. A statistical analysis of the data generated from this survey is not presented at this time; however, such an analysis will be included in the final summary report when data from all nine Phase III surveys are available.

The area sample (F-2) collected in the midst of several heavy fraction pumps showed a cumulative PAH concentration of 202.2 $\mu g/m^3$ with 15 PAHs identified; both of these figures were the highest of the samples collected at this refinery during this phase. Results for the other area sample, collected near the FCCU charge pumps, was 12.1 $\mu g/m^3$ with 12 PAHs identified.

B. Deasphalting Unit

Table VI-5 gives a summary of personal monitoring results for the three workers at the deasphalting unit. These values are again average cumulative PAH concentrations for the two sampling days. These PAH values were higher than expected based on Phase II area results. The number of workers was small at this unit and unfortunately one of the samples was lost, reducing the total number of personal samples to five. The samples varied greatly between workers and between days. Both assistant operators performed similar duties yet Assistant Operator 1 was exposed at much

higher levels than Assistant Operator 2 (35.5 versus 2.5 $\mu g/m^3$). It should be noted that the first assistant operator did repair work on a gasoline-powered internal combustion engine (not part of the refinery equipment) for several hours on the day yielding the highest PAH results (49.8 $\mu g/m^3$). The operator who spent about 85% of his shift inside the positive-pressure control room was exposed at much higher concentrations the first day (20.7 versus 3.4 $\mu g/m^3$). Specific operational or environmental conditions could not be identified to explain the differences.

TABLE VI-5. Personal Monitoring Results - Deasphalting Unit

	NO. OF SAMPLES	$\bar{X}(\mu g/m^3)$	NO. OF PAHs
Operator (inside)	2	12.1	4-5
Assistant Operator 1	2	35.5	4-10
Assistant Operator 2	1	2.5	5
TOTAL	5	19.5	4-10

Results of the two area samples collected at this unit were 41.2 $\mu g/m^3$ (7 PAHs) at the charge pumps and 28.9 $\mu g/m^3$ (12 PAHs) at the asphalt pumps. The results of these area samples, as well as the personal samples, showed that naphthalene represented a large percentage of the total PAH content.

C. PAH Distribution

Table VI-6 shows the percent distribution of PAHs found at the two process units and upwind location by compound ring number. As the table indicates, in all locations, at least 92.0% of the PAHs found were the lighter molecular weight, 2-ring compounds. In the deasphalting unit almost 99% of the PAHs were the 2-ring compounds, especially naphthalene. Naphthalene and its two methyl derivatives were the compounds found in highest concentrations at the FCCU No. 1232.

TABLE VI-6. Distribution (%) of PAHs Found by Ring Number

RING NO.	FCCU 1232	DEASPHALTING	UPWIND
2	92.0	98.9	100
3	7.2	1.0	0
4	0.8	0.1	0
5	0	0	0
6	0	0	0
7	0	0	0

D. Particle-Size Distribution

Table VI-7 shows the particle-size distribution of the four total particulate samples collected alongside the PAH area samples. The samples were consistent in that the majority (at least 92.6%) of particles sized were 1.5 μm or less and no collected particles were greater than 5.9 μm. Three of the samples did not have any particles sized greater than 2.9 μm. All collected particles were well within the respirable-size fraction.

TABLE VI-7. Particle-Size Distribution (%) of Total Particulate Area Samples

PARTICLE SIZE (μm)	SAMPLE NUMBER			
	311	317	359	367
0.4-0.7	65.3	59.3	71.1	78.7
0.7-1.0	17.8	26.3	24.5	9.0
1.0-1.5	9.6	13.5	4.1	10.0
1.5-2.1	5.5	1.0	0.3	2.0
2.1-2.9	1.3	--	--	--
2.9-4.2	0.1	--	--	--
4.2-5.9	0.5	--	--	--

VII. CONCLUSIONS

The Phase II results for this Gulf Oil refinery were consistent with those of the other two surveys in this phase. The fact that the PAHs were the only group of compounds sampled for in Phase II that were consistently found in the area samples should not rule out the presence of the other compounds or classes of compounds. It must be remembered that only a small number of three process units was sampled, and that the number of samples collected was limited. Even though the other potential hazards are not being studied in Phase III of this project, the possibility of their presence in petroleum refineries certainly still exists. A complete summary of the results from all three Phase II surveys is presented in the Phase II Report (November 1979).

Results of personal and area air samples collected during this Phase III survey clearly indicate that workers at FCCU No. 1232 and the deasphalting unit of this refinery are exposed to a number of PAHs, generally at low $\mu g/m^3$ concentrations. In attempting to draw conclusions from this survey, one must keep in mind that the samples were collected over two work shifts during 2 consecutive days. The limitations of such a sampling schedule are recognized; however, there were no unusual operational or environmental conditions during the survey that would cause one to believe that these results were not representative of these units.

The PAH area and personal sampling results from the deasphalting unit were higher than expected based on Phase II area sampling performed at this and two other refineries. In fact, the personal monitoring results (mean cumulative PAH concentration) for this unit over the two sampling shifts were over 30% higher than comparable results from FCCU No. 1232 (19.5 versus 14.6 $\mu g/m^3$). The average number of PAHs identified per sample was higher for the FCCU samples (7.6 versus 5.6 $\mu g/m^3$). It should be noted

when comparing units that many more personal samples were collected at the FCCU (16 for eight workers) than at the deasphalting unit (five for three workers).

The FCCU personal samples showed that workers assigned to the "cat side" of the unit (including those assigned to both sides) were exposed to higher PAH concentrations and more different PAHs than those workers assigned to the recovery side of the unit. This had been anticipated because the process streams containing the heavy petroleum fractions are confined to the "cat side" of the unit. The results for the two inside operators who spend almost 95% of their shift inside the control room (located in the "cat side" of the unit) were higher than expected. The mean cumulative PAH concentration for these two was higher than that for the recovery-side outside operators and about one-half of that for the "cat side" outside operators. Such trends were not indicated from the small number of personal samples collected at the deasphalting unit.

There were wide variations at both units between the duplicate personal samples collected on consecutive day shifts. At FCCU No. 1232, the results were consistently higher on the second sampling day, while at the deasphalting unit, the results were higher the first day. These variations could not be explained by observed differences in work assignments or any unit or environmental conditions.

The purpose of the limited area sampling at FCCU No. 1232 and the deasphalting unit was to collect samples in areas suspected of having relatively high PAH concentrations, to check suspected major PAH emission sources and to compare concentrations and PAH distributions with the personal samples. It was anticipated that the area samples would be considerably higher than the personal samples. This was not always the case; although one FCCU area sample was extremely high compared to other samples, several personal samples at both units were just as high or higher than the other area samples. This, in addition to the PAH levels found for those workers who do not work in high PAH emission areas (control room operators and recovery side operators), indicates that PAHs are not restricted to the areas around major emission sources but are probably widespread throughout many areas of these units.

As expected from Phase II results, the majority of PAHs identified during Phase III were the lighter 2- and 3-ring compounds. At least 92.0% of the PAHs in the samples from both units were the 2-ring compounds and at least 99.2% were 2- or 3-ring compounds. In the deasphalting unit, 2-ring compounds comprised 99% of the PAHs; of these, naphthalene was the predominant compound.

Several of the PAHs identified as being present at this refinery are associated with some degree of cancer-causing potential. However, the lack of existing definitive toxicologic and epidemiologic studies make an assessment of the actual cancer hazard of this group of compounds outside the scope of this study.

The particle-size distribution of the total particulate samples showed that all particles collected were well within the respirable-size fraction (<10μm). These sized particles cannot be directly correlated with the PAH levels found in the area PAH samples. However, airborne PAHs are associated with particulates, and the particle sizing results do indicate that the airborne particulates at the site of the area PAH samples were of respirable size.

Much of the significance of the data generated during this survey will not be evident until Phase III is completed. At that time the concentrations, PAH distributions, and general tendencies noted at this refinery will be compared for consistency with the other study refineries in the final summary report.

APPENDIX

Attendees of Opening Conferences

Phase I

Enviro Control, Inc.	
Stan Futagaki	Senior Industrial Hygienist
Dewey Cubit	Senior Industrial Hygienist
Samuel Kaplan	Senior Industrial Hygienist
NIOSH	
Clinton Cox	NIOSH Project Officer
Barry Palley	Chemical Engineer
Gulf Oil	
George Rideout	Supervisor, Accident and Fire Prevention
Douglas Davis	Corporate Industrial Hygienist
Michael Juba	Corporate Industrial Hygienist

Phase II

Enviro Control, Inc.	
Stan Futagaki	Senior Industrial Hygienist
Edward Haggerty	Industrial Hygienist
NIOSH	
Clinton Cox	Project Officer
Gulf Oil	
George Rideout	Supervisor, Accident and Fire Prevention
John Duffy	Safety Inspector
Michael Juba	Corporate Industrial Hygienist

Phase III

Enviro Control, Inc.	
Stan Futagaki	Senior Industrial Hygienist
Robert Reisdorf	Industrial Hygienist
NIOSH	
Clinton Cox	Project Officer
Gulf Oil	
George Rideout	Supervisor, Accident and Fire Prevention
Jim Stockdale	Maintenance employee
Michael Juba	Corporate Industrial Hygienist