Phase III Survey Report #2

WORKER EXPOSURE TO POLYAROMATIC HYDROCARBONS AT SELECTED PETROLEUM REFINERY PROCESS UNITS

LOCATION OF SURVEYS:

Sun Oil Refinery

Tulsa, Oklahoma

DATES OF SURVEYS:

17-20 April 1979
3-5 December 1979

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Worker exposures to polyaromatic hydrocarbons (PAHs) were surveyed at Sun Oil Refinery (SIC-2911) in Tulsa, Oklahoma from April 17 to 20, and December 3 to 5, 1979. The refinery employed about 850 workers. Personal and area air samples were collected on silver membrane filters and were analyzed for 23 individual PAHs by gas chromatography and mass spectrometry. All samples contained detectable amounts of PAHs. Personal exposures to PAHs ranged from 1.4 to 70.8 micrograms per cubic meter, and most of the PAHs were 2-ring compounds. Naphthalene (91203) and its two methyl derivatives were the compounds found in the greatest concentrations. The authors conclude that workers at this refinery are exposed to numerous PAHs.

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ABSTRACT

A Sun Oil refinery was surveyed during both Phases II and III of this NIOSH-sponsored study characterizing worker exposure to suspected carcinogens in petroleum refineries. In the Phase II industrial hygiene survey, area air samples were collected at the catalytic cracker, delayed coker, asphalt blowing and deasphalting units 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 the catalytic cracker and delayed coker, and area samples only in the asphalt processing units. 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 39 of the personal and area air samples had detectable quantities of at least seven PAHs or groups of PAHs with the cumulative PAH concentration for individual samples ranging from 1.4 $\mu g/m^3$ for one area location in the deasphalting unit to as high as 70.8 $\mu g/m^3$ for a personal sample from one of the operators at the catalytic cracker. The upwind boundary sample was about 1 $\mu g/m^3$.

This report was submitted in fulfillment of NIOSH Contract Number 210-78-0082 by Enviro Control, Inc. under the sponsorship of the National Institute for Occupational Safety and Health (NIOSH).

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1. 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 (FCCU), the delayed coker, 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 study process units.

- Phase III: The objective of this main phase of the study is to characterize worker inhalation exposure to PAHs in the 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 Sun Oil refinery at Tulsa, Oklahoma was one of the three refineries visited as part of Phase II and was revisited as part of Phase III, which is currently in progress. This report presents the information and air-sampling data collected during those two surveys.

The Phase II survey was conducted from April 17-20, 1979. The objective of this survey was to collect a series of area air samples for PAHs, aromatic amines, trace metals, nickel carbonyl, and nitrosamines in the delayed coker unit, FCCU, and asphalt processing units (deasphalting and asphalt blowing). Initial contact for this visit (and the Phase III visit) was made through the corporate Director of Health, Safety, and Security. All subsequent arrangements were made through the refinery Safety Engineer.

The 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 two representatives from Enviro described the project, the status, and the specific objectives of the survey; a tentative schedule was agreed upon for the 4 days. After the opening conference, the survey team conducted a walkthrough of the delayed coker and asphalt blowing units.

The delayed coker and the FCCU were sampled during the day shifts of the second and third days, while the asphalt blowing and deasphalting units were sampled during the day shift of the fourth day. Approximately 40 area samples were collected over the 3 days for the various compounds.

This Sun Oil refinery was revisited from December 3-5, 1979, as part of Phase III of this project. The objective of this survey was to monitor worker exposure to PAHs at the same four process units as the previous phase through a program of personal and area sampling. A brief opening conference was held the morning of December 3 with representatives from the refinery, NIOSH and Enviro (list of attendees in Appendix). As in the previous visit, the representatives from Enviro described the status of the project and the specific objectives of this Phase III survey. After the meeting, the survey team conducted a brief walkthrough of the four process units to be sampled. At the FCCU and delayed coker, the Enviro industrial hygienists explained to the employees the sampling to be performed. During the day shifts of the second and third days, area and personal sampling for PAHs were conducted at the FCCU and delayed coker unit. Only area samples were collected in the asphalt processing units.

II. REFINERY DESCRIPTION

This Sun Oil refinery is located in Tulsa, Oklahoma along the bank of the Arkansas River. With its crude capacity of about 95,000 bbl/day, this refinery is classified as a "medium-size" refinery for the purposes of the study. Since Sun 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 1913, is spread out over approximately 750 acres and at the dates of the surveys was processing about 88,000 barrels of crude a day. A full line of petroleum products is produced including:

- propane
- butane
- gasolines
- jet fuel
- fuel oils (#1, #2)
- asphalt
- coke
- lube oils
- waxes
- kerosene
- Diesel fuel
- petrochemicals (benzene, xylene, toluene, cyclohexane)

This refinery produces over 300 different types of waxes and is also one of the largest producers of lube oils.

The crude refined here, which is primarily domestic, is categorized as a "sweet" (0.2% sulfur by weight), "mixed base" (containing both paraffins and naphthenes) crude with an API Gravity Index of about 40. All of the crude, which originates from Oklahoma, Texas, and a small percentage from foreign sources, is received by pipeline. Most of the gasolines and fuel oils produced are shipped by pipeline with trucks and railcars also being used, especially for coke and asphalt.

The major process units at the Sun refinery include:

- crude distillation unit
- delayed coker
- continuous asphalt blower
- unifiner
- catalytic reformer
- catalytic isomerization unit
- FCCU
- HF and H_2SO_4 alkylation units
- lube extraction and hydrogenation units
- propane deasphalting unit

Almost every major process unit has its own control room. Figure II-1 shows a rough refinery plot plan of the major units.

There are approximately 850 employees including maintenance and administrative personnel. Most of the routine maintenance activity is performed in-house; contractors are brought in for turnarounds and other major maintenance work. The production units operate 24 hours a day over three work shifts, 7 days a week.

The supervisor of personnel and safety heads a refinery safety department that includes:

- a supervisor of fire and safety
- a safety engineer
- a chief safety inspector
- four fire marshals
- six firemen

Although routine industrial hygiene sampling is not performed at this refinery, the safety engineer, who is responsible for industrial hygiene, is currently developing a sampling program. The corporate industrial hygienist also occasionally performs sampling at this refinery.

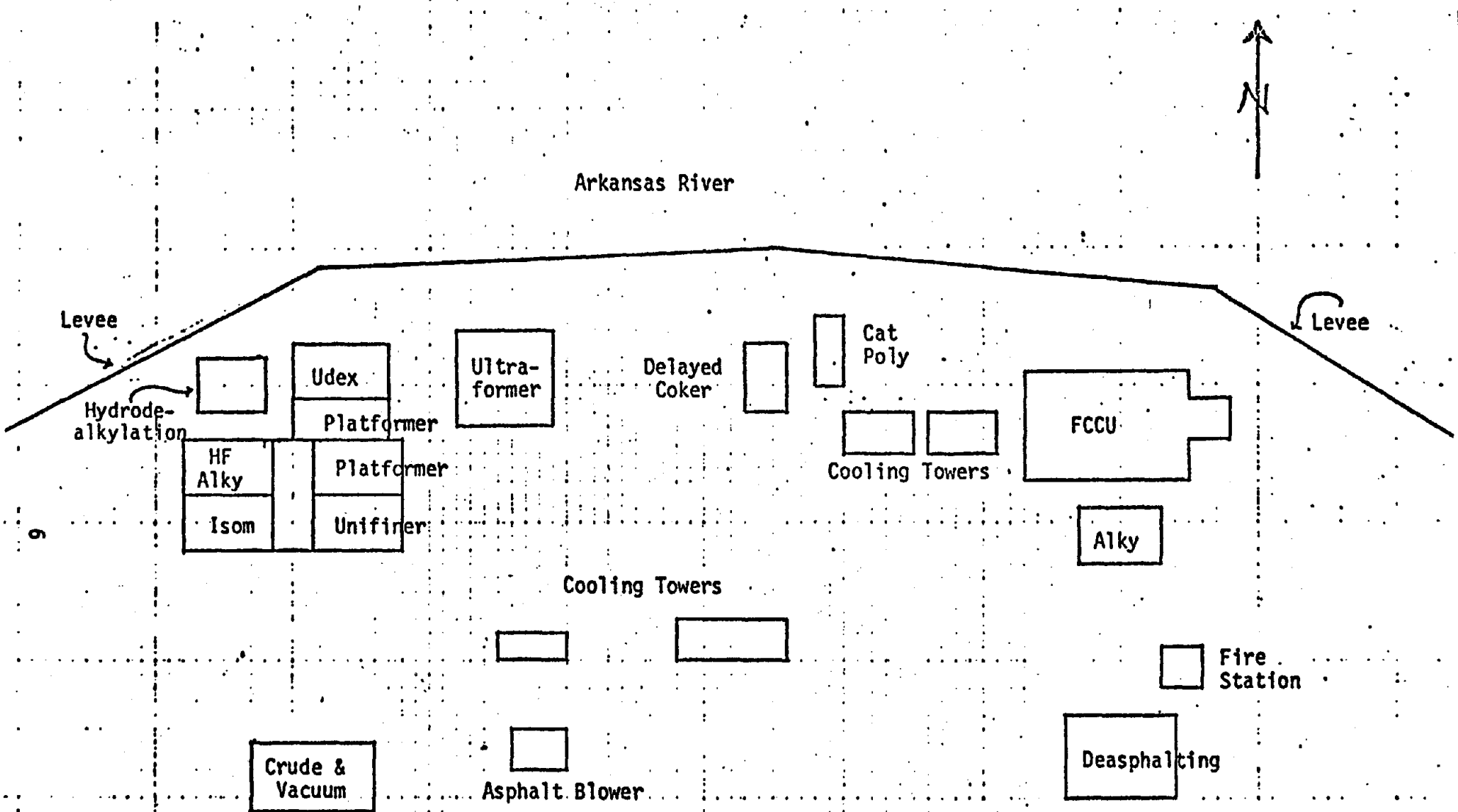


FIGURE II-1. Refinery Production Area

As part of good industrial hygiene practice, the use of protective clothing (e.g., hard hats, safety shoes, gloves, eye protection) and equipment is emphasized. While eating is allowed in most control rooms, smoking is permitted only in designated areas away from the production units. Each unit operator is thoroughly trained on the unit equipment, operations, and associated safety hazards. The practice of good personal hygiene such as the washing of hands before eating is also encouraged. 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 also promptly carried out by the unit operators or in-house maintenance crews.

There is a medical doctor on the premises 5 days a week from 0900 to 1700, and two nurses 5 days a week, one from 0600 to 1400 and the other from 0900 to 1800. The fire department personnel are trained in first aid for periods when the doctor or nurses are not on duty. All of the production workers are given preplacement medical examinations and annual examinations are available.

III. STUDY PROCESS UNITS

FLUID CATALYTIC CRACKER UNIT (FCCU)

A. Unit and Process Description

The FCCU is located in the northeast section of the refinery's main production area (Figure II-1) about 600 feet east of the delayed coker and polymerization units and just north of the No. 1 alkylation unit. A levee runs along the north and northeast boundaries protecting the unit and the refinery from the Arkansas River. This FCCU was built in 1949 and the CO boiler was added in 1964. Several other modifications have been made, such as adding the various cyclones for the regenerator flue gas. The current production capacity of this unit is about 30,000 bbl/day.

Figure III-1 illustrates the layout of this unit which occupies an area about 400 x 225 feet. The side-by-side reactor/regenerator (R/R) structure is located east of the fractionator and control room. The catalyst storage and CO boiler are located east of the R/R structure. The main pump area is located just north of the control room building, and the gas recovery area is located farther west.

Fresh feed for the FCCU consists of soft wax from the lube oil dewaxing plant, low pressure distillate from the coker unit, and atmospheric and vacuum gas oils. This feed, preheated by one of the two gas-fired charge heaters (light and heavy charge heaters), plus heavy gas oil and slurry recycle from the fractionator are mixed with the hot catalyst in the two risers leading to the reactor. The catalytic cracking takes place in the risers as well as in the reactor. The catalyst used at the Sun refinery is a synthetic zeolite common to other FCCUs studied 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 stripped with steam of any remaining oil and delivered to the regenerator through the "spent catalyst leg". In the regenerator, the catalyst is reactivated by oxidizing the accumulated carbon at a temperature above 1000°F (538°C). The flue gas from the regenerator goes through a third-stage cyclone

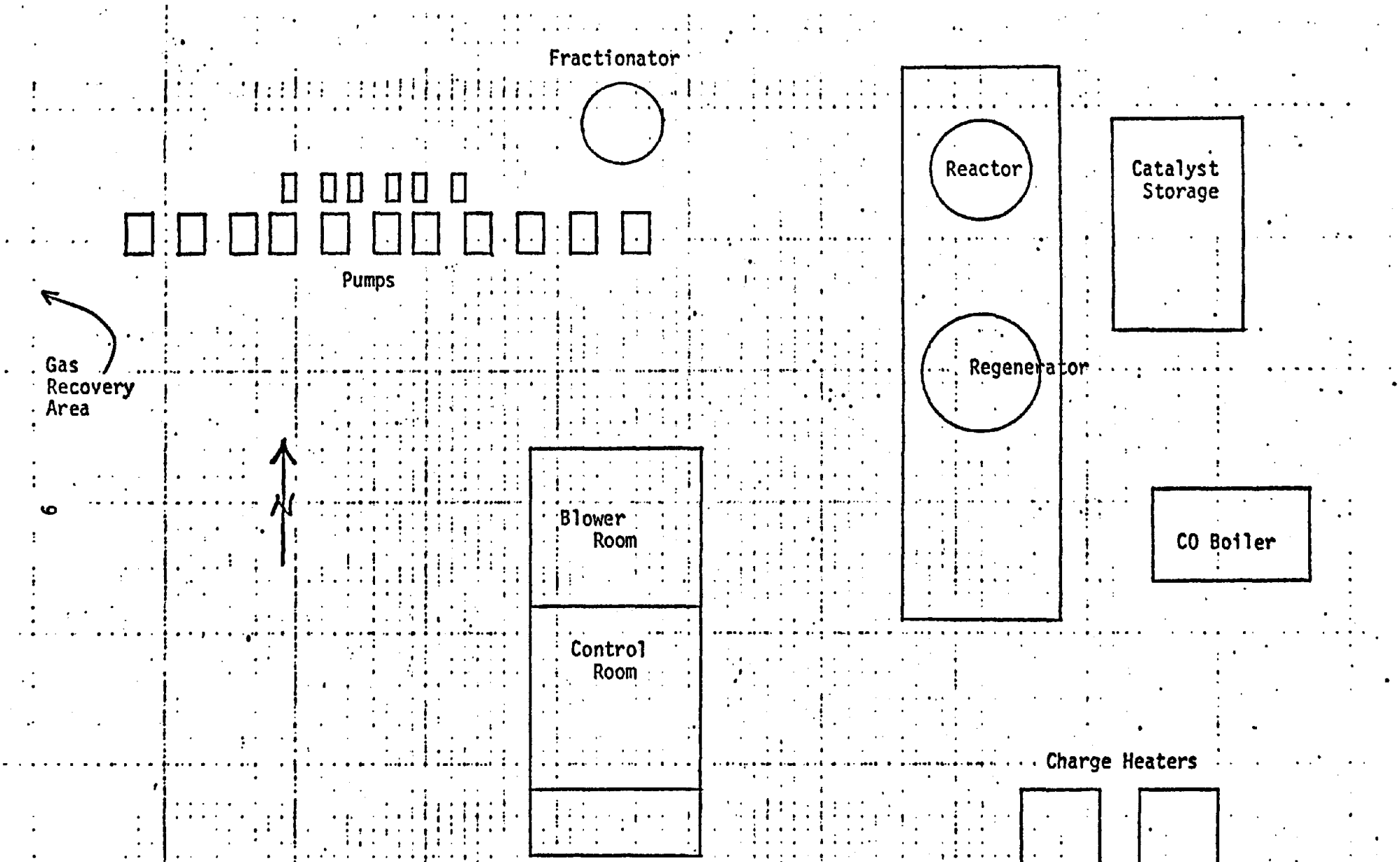


Figure III-1. FCCU

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
- butane
- gasoline
- olefin feed for the alkylation units
- light cat cycle oil
- heavy cat cycle oil
- decanted oil

B. Workforce

There are at least five workers assigned to the FCCU full time during each shift. This includes the chief process operator (CPO), two control room operators, and at least two (outside) process operators. Normally there are one or two additional process operators to assist in the outside operations. During both surveys, there was one additional process operator, making a total workforce of six per dayshift. Following is a brief description of the duties of these six full-time shift personnel.

- Chief process operator: Supervises the overall unit operations. The CPO normally spends the majority of his shift outside the control room providing direction and assistance to the other operators in both the gas recovery and main production areas of the unit.

- Control room process operators (2): Both spend essentially 100% of their shift inside, monitoring and logging in the various meters and charts on the control board. They work closely with the CPO and other process operators to ensure smooth operating conditions.

- (Outside) process operators (3): One process operator is responsible for the CO boiler, R/R structure, and the fractionator; another is reponsible for the gas recovery side which includes the absorber, stripper, deethanizer, air blowers, and compressors; and the third is designated a roving process operator responsible for providing overlap coverage to the other two. They spend 80-90% of their shift outside in the production area. Every 4 hours (twice/shift) they make complete rounds of their respective areas for meter and gauge readings and visual inspection. The quality of the catalyst is checked twice per shift and process stream samples are usually collected during the day shift.

C. Exposure Control Measures

The exposure control measures used at this FCCU are quite typical of those observed at the other FCCUs studied during this project. The primary control measure is a closed-system process which limits exposure to products, by-products, and intermediates. Important also 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 sampling of the various streams, maintenance and housekeeping activities, fugitive emissions, and the regenerator flue gas.

Process stream samples are normally collected once a day (day shift) for the light and heavy oil charge, decanted oil, slurry recycle, light cat cycle oil, and low pressure distillate. The spigot-and-bottle method is used 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. The ground level of the unit is constructed of concrete and the pump area has a sewer system which simplifies cleanup procedures. The refinery has its own craft maintenance crews (e.g., pipefitters, electricans) that provide preventive and repair services. The last major turnaround for this unit was in the middle of 1978.

Hard hats, safety shoes, and rubber gloves with cotton lining are routinely worn by workers at this unit. Safety glasses are furnished by the company and used on a voluntary basis. Coveralls are not provided and are not normally worn. Ear protection is used in the compressor room and fractionator/pump area. There are no routine operations that require the usage of respirators; however, air-purifying and self-contained breathing air respirators are available. These respirators are maintained by the refinery safety department.

The areas of the unit handling heavy fractions, which are more likely to contain the PAHs, are in fairly open areas, minimizing potential vapor accumulation. Several of the heavy gas oil, slurry recycle, and decanted oil pumps are located very close together near the fractionator tower. This is an area where PAH concentrations might be elevated. The air-conditioned control room which is not under positive pressure is occasionally downwind of the R/R or heavy fraction pumps.

The flue gas from the regenerator goes through a series of cyclones to remove catalyst fumes and is then burned in the CO boiler with an auxiliary fuel. The CO boiler not only removes carbon monoxide from the flue gas, but also many hydrocarbons, making the effluent suitable for discharge to the atmosphere.

DELAYED COKER UNIT

A. Unit and Process Description

The delayed coker unit, as shown in Figure II-1, is located on the northern edge of the refinery near the river and levee. Several units including a catalytic reformer, two platformers, an HF alkylation, and an isomerization unit are within 200 yards to the west. Just to the east is the catalytic polymerization unit and to the south are numerous small storage tanks. This coker unit has two 100-foot drums with a daily production capacity of about 200 tons.

The unit, which was built around 1955, is spread over an area of about 300 x 225 feet (Figure III-2). The ground level of the majority of the unit is constructed of concrete. The air-conditioned control room is part of a larger one-story brick building used for storage and light maintenance; this control room is also used for the polymerization unit located just to the east. The locker and shower facilities used primarily by the coke cutters are located in a separate small brick building on the south side of the coker tower. The coker tower is an open, multi-level structure that includes the two drums, an elevator, and the penthouse at the top. Railroad cars can be positioned directly beneath the bottoms of the drums to provide direct loading as the coke is cut.

The gas-fired charge furnace is located just to the north of the control room and the fractionator near the coke drums just to the south. The quench tank (not on Figure III-2) for condensing the steam from the steam-out operation is located south of the elevator.

"Sponge" or #2 grade coke is the only type of coke produced at this unit. The charge stock is made up of bottoms from the deasphalting and vacuum units. The incoming charge either goes to the feed surge drum where it is stored until needed or to the fractionator. Prior to going to the fractionator, the charge can pass through the gas-fired preheat furnace if necessary. The light ends are flashed off in the fractionator and eventually go the the FCCU gas recovery. The bottoms from the fractionator are pumped through the convection and radiant sections of the furnace heating the charge to about 900°F (482°C). The charge then goes to one of the two coking drums. Each drum has a 48-hour cycle with coke formation

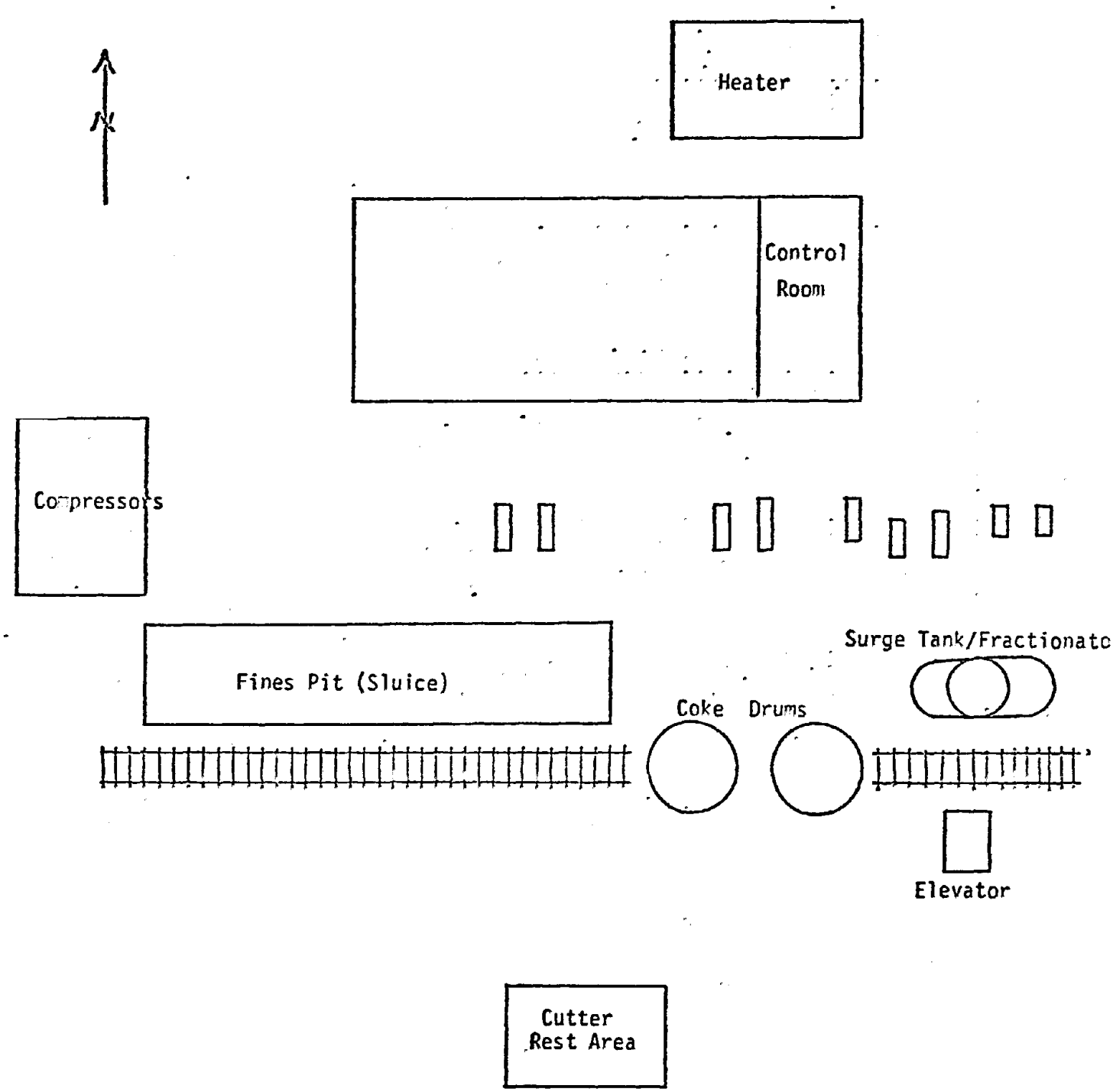


Figure III-2. Delayed Coker Unit

lasting about 24 hours. Since the drums work as a pair, cutting of one drum occurs every 24 hours (about 0700 every morning). The lighter vapor fractions of the thermal cracking operation are removed from the top of the drum and sent to the fractionator where the various products are separated and eventually recovered. Besides coke, products from this unit include gasoline, overhead gases, unstabilized gasoline, and gas oil.

The complete cycle of each drum from heating to cutting is 48 hours. About 9 hours before the cutting operation is scheduled, coke formation is stopped by switching the feed valve to the other drum. In 30 minutes, steam is introduced into the drum to cool it. This lasts about 5 hours and then water is added to further cool the drum. Nine hours after the valve is switched, the top and bottom of the drum are opened and an initial hole is bored through the coke from the top with a high-pressure hydraulic bit (> 2,000 psi). The bit is changed to a revolving-head type and the coke is cut from the bottom up. The coke falls directly into a railcar stationed below the drum bottom. A motorized winch is used to move the car to ensure even loading. The actual boring and drilling lasts from 3 to 4 hours.

After cutting is completed, the top and bottom of the drum are replaced; the drum is pressure tested for seal, heated, and is ready when the charge valve is switched from the other drum to begin coke formation.

B. Workforce

The workforce for the coker unit is divided into two groups, the operations group and the coke-cutting group. The two-person operations group works the normal 8-hour shift; following is a brief description of their job activities.

- Chief process operator (CPO): Is in charge of the overall unit operations. The CPO normally spends 1-2 hours per shift outside checking certain equipment or making visual inspection of the unit. The CPO can assist the process oeprator in tasks that require two, such as troubleshooting. Most of the inside time is spent performing normal board operator tasks.

- Process operator: Performs most of the routine outside tasks such as visual inspection, meter and gauge readings, valve switching, steam pressure testing of coke drums, starting and shutting down pumps, lubricating and oiling pumps and compressors, and sample collecting (fresh feed, gas oil, and slop samples once per shift). The process operator spends almost all of the shift outside.

The coke-cutting group is normally made up of the head cutter and two helpers, with one of the three performing drilling each cutting shift. During the Phase III survey, there was an additional helper being trained. This group works only during the day shift and is responsible for cutting and cleanup operations. Cutting normally takes 3-4 hours; cleanup takes an additional 2 hours.

- Head Cutter: Is in charge of the coke-cutting operation. He performs the drilling or assists the helper. During the Phase III survey, he was training a new helper and spent all of his shift below at ground level.

- Helpers: When acting as the driller (as during Phase III), one helper spends 30-40 minutes helping to open the top and bottom of the drum and then goes to the penthouse at the top where he operates the drilling controls. It takes about 40 minutes to make the initial "bore through" and then the bit is switched for the actual cutting, which lasts about 3 hours more. He then helps in closing the drum and in general cleanup operations. The non-driller helper(s) assists with opening and closing the drum and positioning the sleeve at the drum bottom. During the rest of the cutting operations, they are below on the ground level or on the first level of the coke tower structure. One helper is positioned in a three-sided shelter open to, and level with, the top of the railcar. From here he regulates movement of the cars (by motorized winch) to allow even loading of the cars. Another helper is also on this level using a long pole to help evenly

distribute the accumulating coke. Cleanup is ongoing during cutting but everyone helps once the cutting is completed. Large coke pieces on the ground are either picked up or shoveled, and the whole area is hosed down to wash smalle coke particles down into the sluice (fines pit).

At the beginning of the day shift, the coke cutters will often report to the control rooms; however, they rarely go back during the shift. They change and shower in their separate locker room building and eat their lunch there. Smoke breaks are taken in an area to the north of the unit.

C. Control Measures

The coke cutting operation is one of the few in a refinery that is not a closed system. Because of this, it is more difficult to minimize worker exposure during this operation. During every cutting cycle the top and bottom of the drum must be opened manually; the coke must be cut by the driller; and the helpers must clean and prepare the fittings, and at this particular unit, ensure that the railcars are properly loaded, and cleanup the coke tower structure and ground area. There are several important advantages and disadvantages concerning worker exposure associated with cutting the coke directly into railcars.

This method using railcars eliminates the necessity of the crane and any other type of loading equipment such as front-end loaders and trucks. However, this method requires that at least one of the helpers be stationed at the drum bottom area to ensure proper railcar loading. This worker(s) is in very close proximity to the falling coke, splashing water, and water mist. The coke at this point has been cooled, and hydrocarbon vapor is not likely. Exposure is more likely to be dermal and to coke particulates.

The opening of the top and bottom of the drum was done efficiently and quickly. The head cutter and two helpers worked as a team to complete both openings in about 40 minutes. After the bottom is dropped, a metal sleeve is positioned directly under the bottom of the drum. This forms a more closed system on this level where the helpers spend a good part of their time during the operation.

The penthouse on the top level is a relatively enclosed one-room building (10 x 20 feet) where the driller operates the overhead drills. There are two circular openings in the roof and several windows; however, natural ventilation did not appear to be good.

Direct loading of railcars normally requires considerable cleanup at the end of each cutting, as was the case at this unit. The tracks have to be cleared of the large coke chunks, and the entire ground area must be hosed down. This takes up to 2 hours.

All workers on this unit wore hard hats, safety shoes, and gloves (rubber with cotton lining). Coveralls were not provided by the employer; normally the cutters put on a jacket or other type of outer clothing in the locker room and showered or washed up at the end of their shift. There were no routine operations that required the use of respirators; however, NIOSH-approved air-purifying and self-contained breathing air respirators were available. The operations crew ate in the control room while the cutters ate and rested in their separate building. Both the control room and the building used by the cutters were air conditioned but not under positive-pressure. Because of the changing wind direction at this refinery, these buildings are occasionally downwind of the coke drums or pumps.

The steam that is used to cool the drums is sent through a quench tank before it is vented to the atmosphere. A flare is available for turnarounds or any other conditions that might require it.

DEASPHALTING UNIT

A. Unit and Process Description

The propane deasphalting unit (PDA), as shown on Figure II-1, is just south of the fire station and about 150 yards south of the No. 1 alkylation unit. It is also about 300 yards east of the asphalt blowing unit. The PDA has two deasphalting towers in the northeast corner of the unit and has a production capacity of about 5000 barrels of asphalt per day.

This unit, which is approximately 20 years old, is spread out over an area of about 250 x 150 feet (Figure III-3). The propane storage tanks are located in the southwest corner; just to the east is the air-conditioned control room, which is part of larger one-story building housing compressor and pump rooms. There are three gas-fired furnaces in the southeast corner of the unit near the asphalt and oil flash towers. The ground level of the entire unit is constructed of concrete.

There are two separate deasphalting processes within this one unit. One process (designated "A" for this report) yields a larger percentage of asphalt than oil. The asphalt is used for asphalt blowing and coke production, and most of the gas oil is used for FCCU charge. The second process (designated "B") yields a smaller percentage of asphalt than oil; the asphalt is sent to the coker, and the oil produced is used for lube oil and wax production.

The feed stock for this unit is reduced crude from the crude unit. The feed is steam heated to operating temperature and fed to the center of the deasphalting towers. Here it comes in contact with liquid propane which has also been steam heated, and the liquid-liquid extraction process takes place. Asphalt is removed from the bottom of the reactors, and the extracted oil (and propane) are removed from the top. The asphalt from both towers passes through separate gas-fired heaters and then to flash drums where most of the propane is removed. The asphalt then goes to the steam strippers to remove any remaining propane and then is pumped to the asphalt blower or coker units.

The oil-propane phase from the "A" deasphalting tower is heated and sent to the oil flash tower where much of the propane is vaporized by indirect steam heating. The remaining propane 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.

The oil-propane phase from the "B" deasphalting tower undergoes a more involved process to separate the propane and oil. There are a series of compressors, settlers, and strippers that separate the oil for use in the lube and wax units.

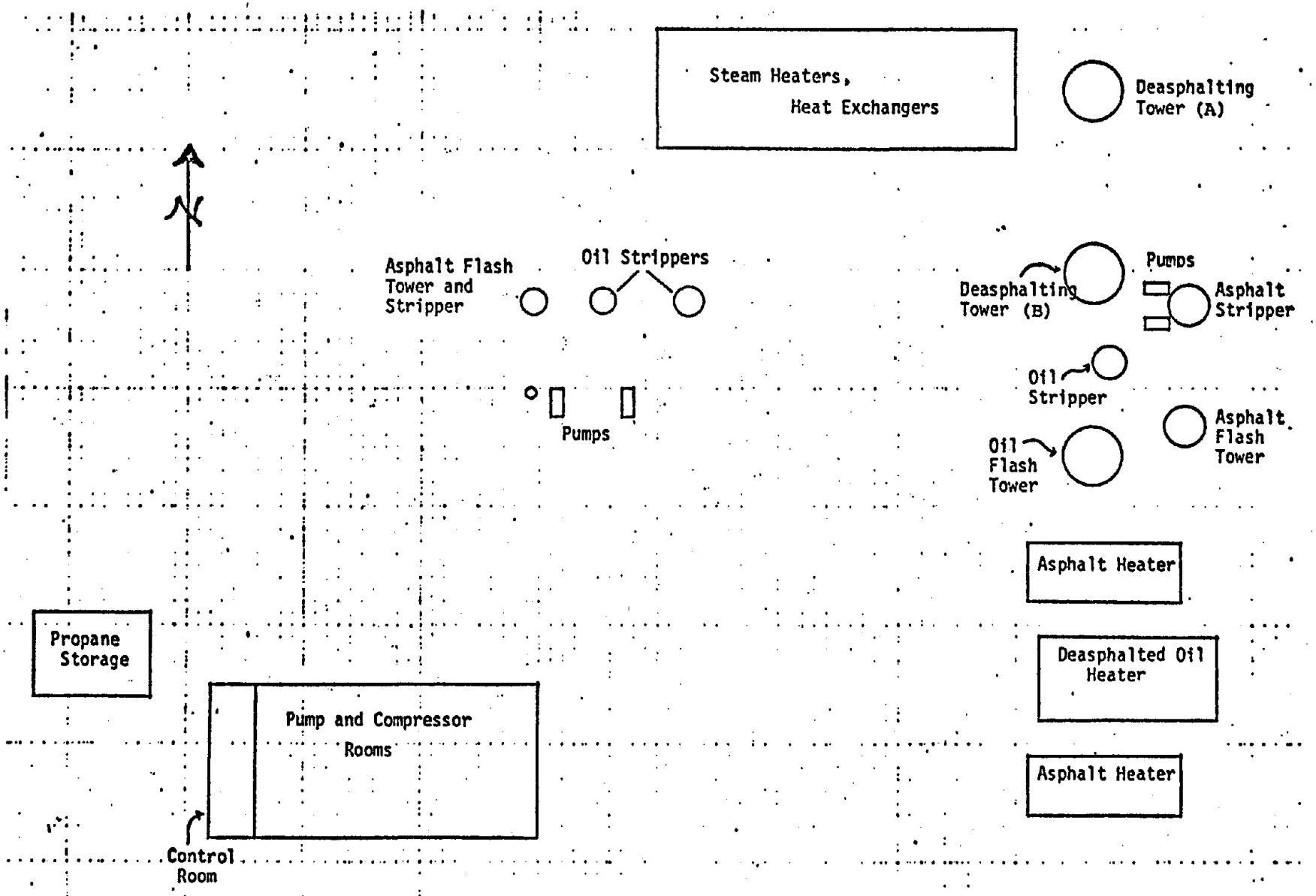


Figure III-3. Deasphalting Unit

B. Workforce

Three workers are assigned to this unit per shift including one inside board operator and two outside operators. Job duties are typical of inside and outside operators on totally enclosed, continuous process units.

ASPHALT BLOWING UNIT

A. Unit and Process Description

The asphalt blowing unit is located about 100 yards east of the crude unit and 100 yards south of a series of cooling towers. There are two blowing towers side-by-side with a maximum capacity of about 6000 barrels of blown asphalt per day. Normal production ranges from 1000 to 4800 bbls/day.

The unit was converted in 1962 from oil distillation stills to the blowing towers. The unit (Figure III-4) is a relatively small, simple unit with main structures that include a small brick control building, the two blowing towers, and a thermal oxidizer unit (incinerator), which was added in 1978 to help control the emissions from the towers. The unit foundation is gravel.

The feed to the blowing towers comes from the deasphalting unit and enters the vertical vessels in the upper half at two or three points. The compressed air passes through a knockout drum to remove any entrained mist and particulates and is discharged into the bottom of the towers. The blown asphalt is pumped to storage tanks.

B. Workforce

This unit requires only two workers per shift, one inside control board operator and an outside operator.

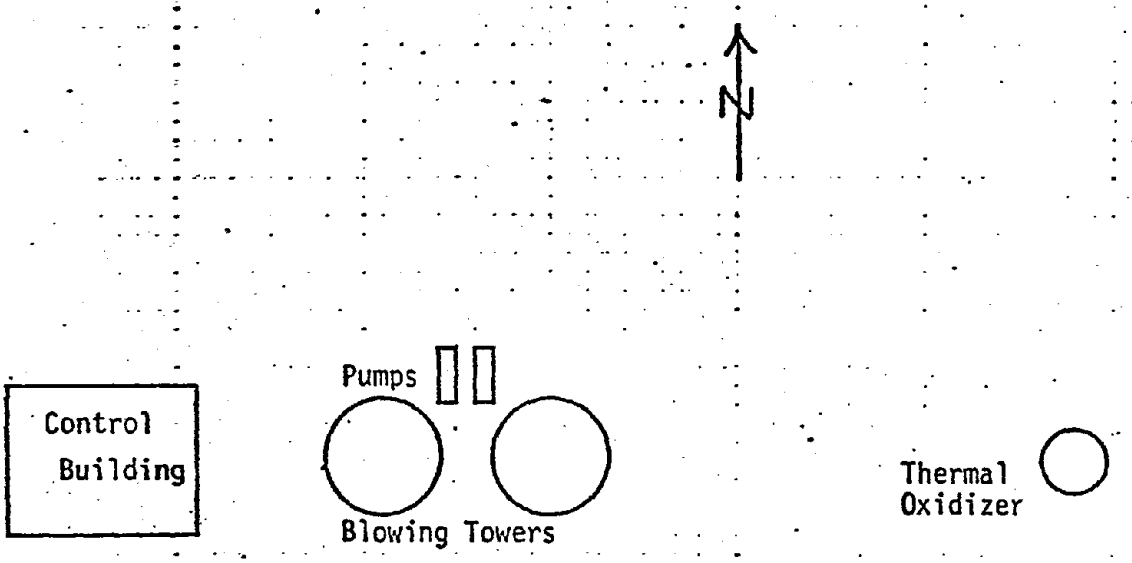


Figure III-4. Asphalt Blowing Unit

IV. 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 Sun 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 18) were partly cloudy skies with the temperatures ranging from 63°F (17°C) in the early morning (0800) to about 71°F (22°C) by afternoon (1400). The relative humidity was 39% at noon and the wind was from the south at 19 mph gusting to 28 mph.

The second sampling day was again partly cloudy but slightly warmer. The temperatures were about 70°F (21°C) at 0830 and 82°F (28°C) by 1400. The relative humidity was 64% at noon and the wind was from the south-southwest at 12-22 mph.

The final sampling day was cloudy with the temperatures ranging from 68°F (20°C) at 0830 to 74°F (23°C) at 1300. The relative humidity at noon was 71% with rain commencing about 1430, as the sampling was being terminated. Winds were from the south-southwest at 14 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. A problem became apparent in that the air flow rate was reduced from about 9.2 ℓ/minute to as low as 3.0 ℓ/minute if the cassette was pressed too firmly down on the critical orifice. This caused the critical orifice to come directly into contact with the support filter pad. This problem was easily alleviated by making a conscious effort not to press the cassette too far down. During sampling, the cassette was wrapped in aluminum foil to minimize photodecomposition of the sample material.

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 27 PAH and azoheterocyclic 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*
15. Chrysene*/Triphenylene
16. Dimethylbenz(a)-anthracene*
17. Benzo(e)pyrene*
18. Benzo(a)pyrene*
19. Perylene
20. Dibenz(a,j)acridine*
21. Dibenz(a,i)carbazole*
22. Dibenzanthracene*
23. Indeno(1,2,3-cd)pyrene
24. Benzo(g,h,i)perylene
25. Anthanthrene
26. Dibenzpyrene*
27. 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.

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

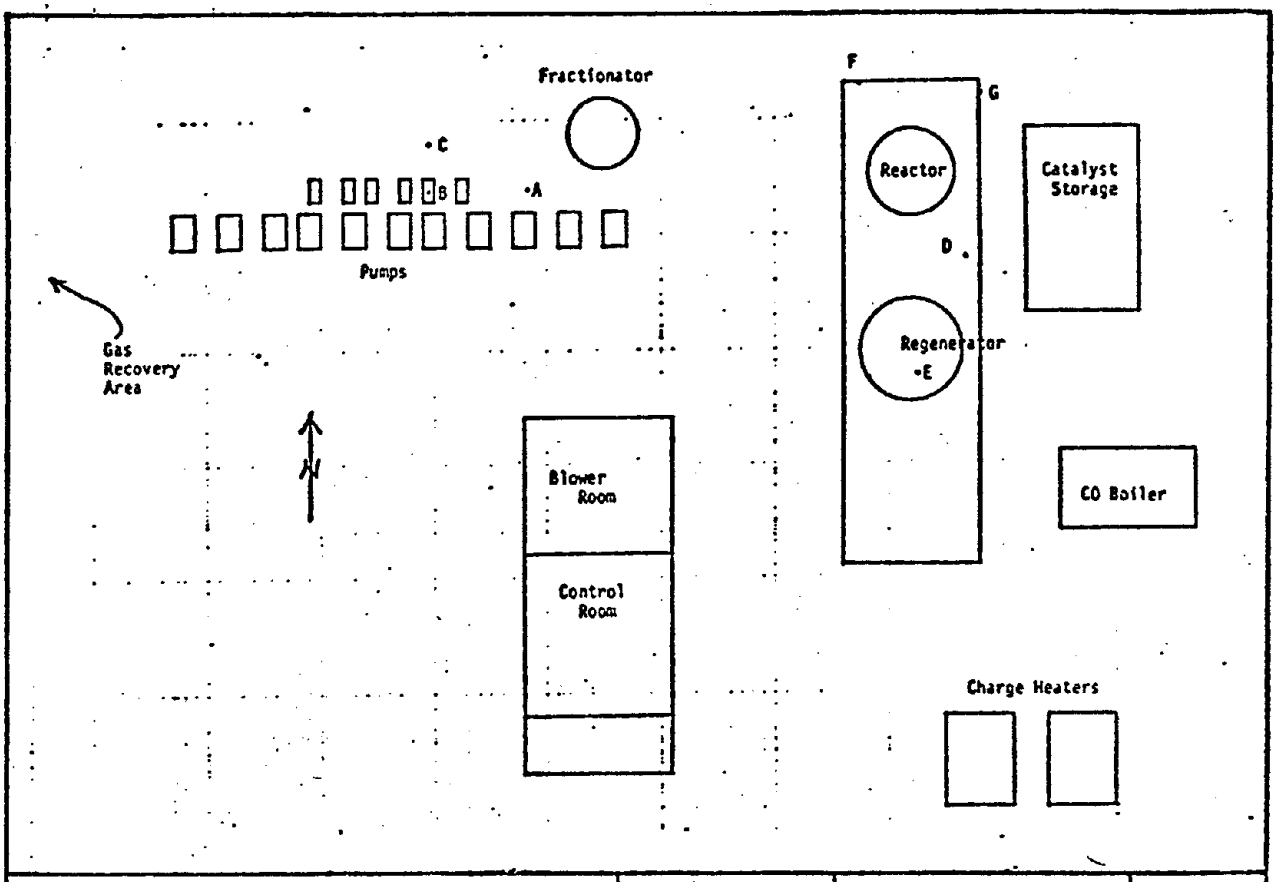
Although aromatic amines are indicated as present in various refinery streams, no information could be found on monitoring data, nor was mention of specific compounds found. Because of this, Enviro attempted in Phase II to identify specific aromatic amines. A limiting factor here was that only seven aromatic amines have established NIOSH sampling and analtyical 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. Aromatic amines were collected on large (850 mg) silica gel tubes. High-flow MSA 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 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 sampling pump set at 2 ℓ/minute, desorbed with solvent, and analyzed by gas chromatography with a Thermal Energy Analyzer.

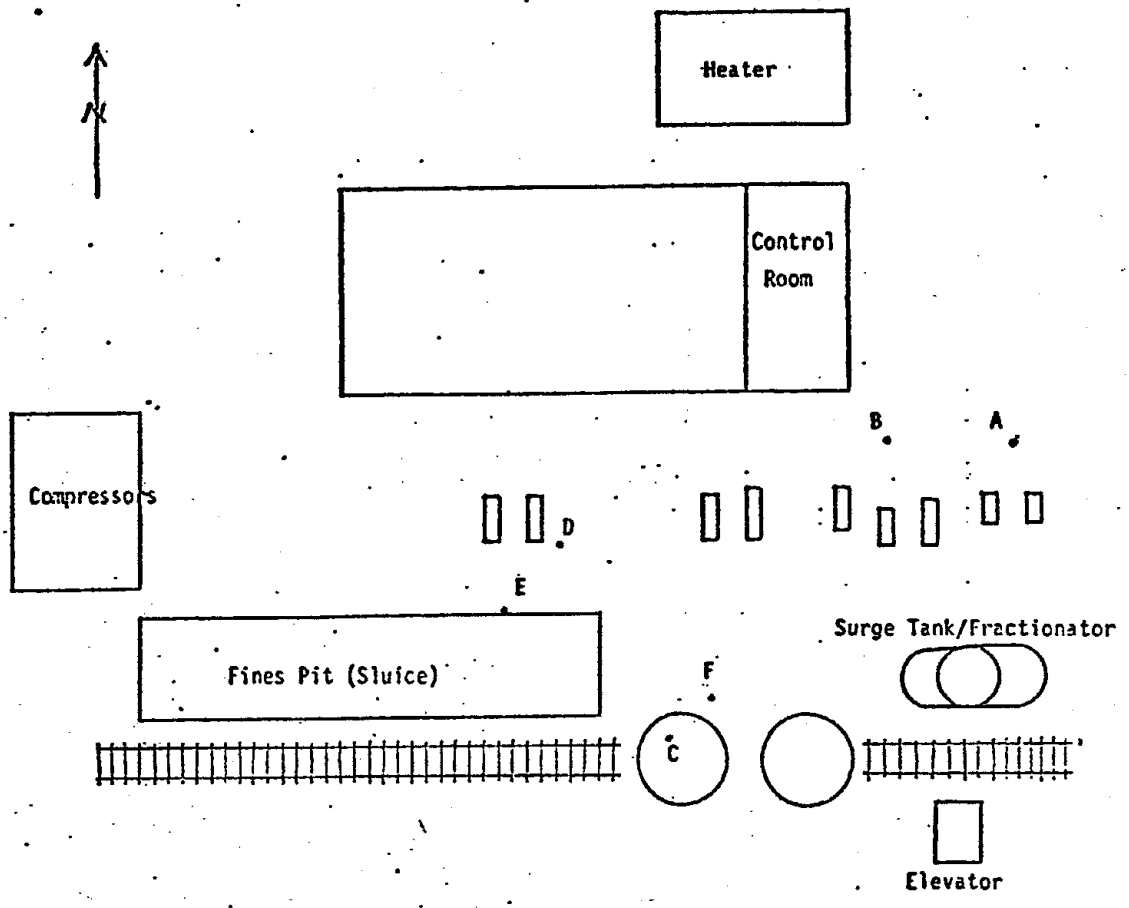
D. Sampling Locations

Figures IV-1 through IV-3 illustrate the various area sampling locations and sample types at the FCCU, coker, and asphalt blowing unit. At the deasphalting unit, only one PAH sample and one aromatic amine sample were collected and analyzed. These were collected on the asphalt pump about 5 yards from the asphalt stripper. An upwind PAH sample was collected on the south side of the asphalt blowing unit on April 20. This location was upwind (south) of the production units; however, there were numerous storage tanks to the south.



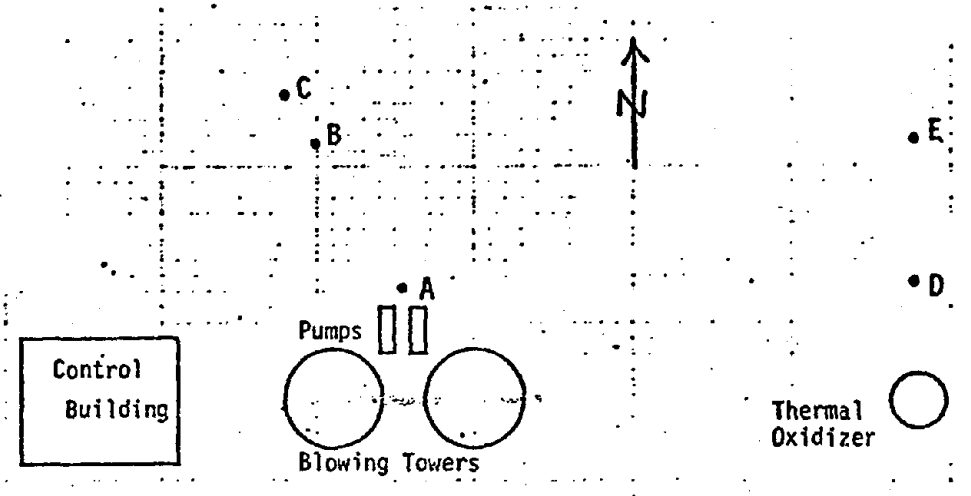
Location	Sample Number	Sample Type	Date
A. Downwind (DW) of decanted oil pump	202 207	Aromatic Amines PAHs	4/18 4/18
B. Slurry reflux pump	204	Nitrosamines	4/18
C. DW of slurry reflux pumps	205 212	Aromatic Amines PAHs	4/18 4/18
D. Between catalyst hoppers and regenerator	203	Trace metals	4/18
E. DW of cyclone	206	Trace metals	4/18
F. NW corner of R/R structure	234 235	PAHs Aromatic Amines	4/19 4/19
G. NE corner of R/R structure	233	PAHs	4/19

FIGURE IV-1. FCCU SAMPLING LOCATIONS



Location	Sample Number	Sample Type	Date
A. Downwind (DW) of furnace charge pumps	209	PAHs	4/18
	210	Aromatic amines	4/18
B. DW of heavy cat cycle oil pumps	211	Aromatic amines	4/18
C. Penthouse (top of coke drum)	221	PAHs	4/19
	222	Aromatic amines	4/19
	223	Nickel carbonyl	4/19
	223F	Trace metals	4/19
	224	Nitrosamines	4/19
D. DW of railcar loading (ground level)	228	Nitrosamines	4/19
	229	PAHs	4/19
	231	Nickel carbonyl	4/19
	231F	Trace metals	4/19
	232	Aromatic amines	4/19
F. Sluicer railing	230	PAHs	4/19
F. Bottom of coke drum	227	Trace metals	4/19

FIGURE IV-2. COKER UNIT SAMPLING LOCATIONS



Location	Sample Number	Sample Type	Date
A. Downwind (DW) of about 4 yards from asphalt pumps	241	Nitrosamines	4/20
	242	Aromatic amines	4/20
	243	Nickel carbonyl	4/20
	243F	Trace metals	4/20
	244	PAHs	4/20
B. DW of valves to coker and tank 193	245	PAHs	4/20
C. Pump to coker	246	Aromatic amines	4/20
	247	Trace metals	4/20
D. DW about 10 yards from thermal oxidizer (T.O.)	248	PAHs	4/20
	251	Nitrosamines	4/20
	252	Nickel carbonyl	4/20
	252F	Trace metals	4/20
E. DW about 20 yards from T.O.	249	PAHs	4/20

FIGURE IV-3. ASPHALT BLOWER SAMPLING LOCATIONS

RESULTS AND DISCUSSION

Analytical results of the area air samples collected at this Sun 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. The only positive result of the aromatic amine samples was a very small concentration of a single aromatic amine found in one FCCU sample. The results of the PAH samples showed that most of the areas sampled at the FCCU and delayed coker unit contained detectable quantities of between 9 and 15 different PAHs (or groups of PAHs) and in quantities that were considerably above those found in the upwind area sample. The PAH concentrations from samples collected at the asphalt blower and deasphalting units were much less than those at the other two study process units and were quite similar to the concentrations from the upwind sample. The following is a more detailed presentation of the Phase II sampling results.

PAHs

Table IV-1 shows the complete results of the PAH samples. The four samples collected at the FCCU had a mean (arithmetic) cumulative PAH concentration of 15.6 $\mu g/m^3$ with 7 to 15 individual PAHs identified. Two samples were collected in the heavy fraction pump area near the fractionator, and two were collected near the reactor/regenerator (R/R) structure. The two samples in the pump area showed the highest cumulative PAH concentrations (28.4 and 32.7 $\mu g/m^3$) of the samples collected at this refinery. The numbers of individual PAHs identified (15 and 11, respectively) in these two samples were also among the highest found at this refinery. The majority of the PAHs identified were the lighter molecular weight, 2-ring (87.5%) and 3-ring (8.8%) compounds. The two samples collected in the area of R/R showed cumulative PAH concentrations of only 1.0 and 0.3 $\mu g/m^3$ with nine and seven individual PAHs identified, respectively. It was unusual to find that in these two samples there were greater quantities of the 3- and 4-ring compounds than the 2-ring compounds. This might be explained by the fact that distribution of PAHs found in samples with such small amounts is normally not as representative of the true distribution as samples with greater amounts.

TABLE IV-1. RESULTS OF PAH AREA SAMPLES ($\mu g/m^3$)**

		FCCU				COKER				ASPHALT BLOWER				D.A.†	UPWIND
Sample Number		207	212	233	234	209	221	229	230	244	245	248	249	254	253
Sample Volume (m^3)		3.1	3.4	3.6	3.6	2.3	1.4	3.8	3.8	2.6	3.5	3.7	3.7	1.2	3.6
Naphthalene*	(2)‡	7.51	10.32	---Δ	---	5.54	1.09	1.16	0.64	0.04	0.03	---	---	0.01	0.01
Quinoline	(2)	2.30	0.26	---	---	0.93	0.17	0.22	---	---	---	---	---	---	---
2-Methylnaphthalene	(2)	6.06	12.50	0.14	---	13.78	2.69	2.75	1.04	0.28	0.15	<0.01	<0.01	0.01	0.04
1-Methylnaphthalene	(2)	6.10	7.44	0.14	---	7.03	1.34	1.71	0.74	0.08	0.11	<0.01	<0.01	0.01	0.04
Acenaphthalene	(2)	0.15	<0.01	---	---	0.12	---	<0.01	---	---	---	---	---	---	---
Acenaphthene	(2)	0.35	---	---	---	0.33	0.03	0.03	0.03	---	<0.01	<0.01	<0.01	---	---
Fluorene	(3)	0.30	0.21	0.16	---	0.34	0.23	0.27	0.16	<0.01	<0.01	<0.01	0.03	0.01	0.01
Phenanthrene/ Anthracene*	(3)	2.02	1.09	0.51	0.13	0.13	0.66	0.47	0.27	---	---	0.05	0.11	0.26	0.06
Acridine*	(3)	1.15	---	0.01	0.01	0.03	---	0.03	---	---	---	<0.01	0.04	0.01	---
Carbazole	(3)	0.63	<0.01	<0.01	<0.01	---	---	---	<0.01	---	---	<0.01	0.01	---	---
Fluoranthene	(4)	0.34	0.02	0.02	0.02	---	---	<0.01	<0.01	---	---	<0.01	<0.01	---	---
Pyrene*	(4)	0.13	0.22	0.04	0.07	---	<0.01	0.02	<0.01	---	---	<0.01	<0.01	---	---
Benzo(a)fluorene/ Benzo(b)fluorene	(4)	---	0.14	<0.01	0.05	---	---	---	---	---	---	---	---	---	---
Benz(a)anthracene*	(4)	1.36	---	---	0.01	---	---	---	0.01	---	---	---	---	---	---
Chrysene/Triphenylene	(4)	---	---	---	---	---	---	---	<0.01	---	---	---	---	---	---
Dimethylbenz(a)-anthracene*	(4)	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Benzo(e)pyrene*	(5)	0.01	---	---	---	---	---	---	---	---	---	---	---	---	---
Benzo(a)pyrene*	(5)	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Perylene	(5)	0.01	---	---	---	---	---	---	---	---	---	---	---	---	---
Dibenz(a,j)acridine*	(5)	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Dibenz(a,i)carbazole*	(5)	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Dibenzanthrecene*	(5)	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Indeno(1,2,3-cd)-pyrene*	(6)	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Benzo(g,h,i)perylene	(6)	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Anthanthrene	(6)	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Dibenzopyrene*	(6)	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Coronene	(7)	---	---	---	---	---	---	---	---	---	---	---	---	---	---
TOTAL		29.4	32.7	1.0	0.3	29.1	6.2	6.7	2.9	0.4	0.3	0.1	0.2	0.3	0.2

* Suggested as having some cancer-causing potential
** Blank values have been subtracted out of data
† D.A. - deasphalting unit
‡ ( ) - ring number
Δ "---" - designates none detected

The four PAH samples collected at the delayed coker unit had a mean cumulative PAH concentration of 11.0 $\mu g/m^3$ with 8 to 11 individual PAHs identified. The sample collected downwind of the heavy fraction pumps again showed the highest cumulative PAH concentration (28.1 $\mu g/m^3$) with nine individual PAHs identified. The other three samples, associated with the actual coke cutting operation (penthouse and downwind of coke loading), showed cumulative PAH concentrations from 2.9 to 6.7 $\mu g/m^3$ with 8-11 PAHs identified. The great majority of the PAHs were the 2-ring (93.9%) and 3-ring (5.9%) compounds.

The five PAH samples collected at the asphalt blowing and deasphalting units had a mean cumulative PAH concentration of less than 0.3 $\mu g/m^3$ with four to nine PAHs identified. These were similar to the results of the upwind sample which showed 0.2 $\mu g/m^3$ and five PAHs.

Aromatic Amines

Table IV-2 shows the results of the aromatic amine samples. Of the 11 silica gel samples analyzed, only one had detectable quantities of any of the seven aromatic amines. This sample, collected in the pump area of the FCCU, showed an air concentration of 0.2 ppm of p-anisidine as a time-weighted average over the sampling period.

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 11 samples analyzed had detectable quantities of this compound.

Trace Metals

Table IV-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 eight area samples analyzed (two from the FCCUs, three from the asphalt processing, three from the coker unit). It should be noted that metal catalysts were not used in the FCCU.

TABLE IV-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-aniline	o-ansidine	p-anisidine	1-naphthyl-amine	p-nitro-aniline
202	FCCU	0.478	<.05	<.05	<.05	<.05	<.01	*0.02	<.05	<.05
205	FCCU	0.488	<.05	<.05	<.05	<.05	<.01	< .01	<.05	<.05
235	FCCU	0.477	<.05	<.05	<.05	<.05	<.01	< .01	<.05	<.05
210	Coker	0.553	<.05	<.05	<.05	<.05	<.01	< .01	<.05	<.05
211	Coker	0.558	<.05	<.05	<.05	<.05	<.01	< .01	<.05	<.05
222A	Coker	0.495	<.05	<.05	<.05	<.05	<.01	< .01	<.05	<.05
222B	Coker	0.495	<.05	<.05	<.05	<.05	<.01	< .01	<.05	<.05
232A	Coker	0.443	<.05	<.05	<.05	<.05	<.01	< .01	<.05	<.05
232B	Coker	0.443	<.05	<.05	<.05	<.05	<.01	< .01	<.05	<.05
242	A.B.	0.501	<.05	<.05	<.05	<.05	<.01	< .01	<.05	<.05
246	A.B.	0.468	<.05	<.05	<.05	<.05	<.01	< .01	<.05	<.05
250	A.B.	0.406	<.05	<.05	<.05	<.05	<.01	< .01	<.05	<.05
258	D.A.	0.500	<.05	<.05	<.05	<.05	<.01	< .01	<.05	<.05

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

TABLE IV-3. RESULTS OF TRACE METAL AREA SAMPLES ($\mu g/m^3$)*

Sample Number	Process Unit	Sample Volume (m^3)	Co	Cr	Ni	Cd	As	Be
203	FCCU	0.796	<3.8	<3.8	<3.8	<0.4	<0.1	<0.1
206	FCCU	0.717	<4.2	<4.2	<4.2	<0.4	<0.1	<0.1
223F	Coker	1.044	<2.9	<2.9	<2.9	<0.3	<0.1	<0.1
227	Coker	0.882	<3.4	<3.4	<3.4	<0.3	<0.1	<0.1
231F	Coker	0.812	<3.7	<3.7	<3.7	<0.4	<0.1	<0.1
243F	A.B. **	0.556	<5.4	<5.4	<5.4	<0.5	<0.2	<0.2
247	A.B.	0.847	<3.5	<3.5	<3.5	<0.4	<0.1	<0.1
252F	A.B.	0.424	<7.1	<7.1	<7.1	<0.7	<0.2	<0.2

*All six metals were not detectable in any of the eight (8) samples; values express detection limits.
**Aspahlt Blowing.

Nickel Carbonyl

Table IV-4 shows the results of the nickel carbonyl analysis. Nickel carbonyl was not detectable in any of the four area samples analyzed (two from the asphalt blowing unit, two from the coker). The minimum detectable concentrations for these samples ranged from 1.4 to 3.5 $\mu g/m^3$ depending on the sample volume.

TABLE IV-4. RESULTS OF NICKEL CARBONYL AREA SAMPLES ($\mu g/m^3$)*

Sample Number	Process Unit	Sample Volume (m^3)	$Ni(CO)_4$
223	Coker	1.044	<1.4
231	Coker	0.812	<1.8
243	Asphalt Blowing	0.556	<2.7
252	Asphalt Blowing	0.424	<3.5

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

Nitrosamines

Table IV-5 shows the results of the nitrosamine area samples. There were no detectable quantities of any of the seven nitrosamines in the five area samples analyzed (one from the FCCU, two from the coker, two from the asphalt blower). The lower limit of detection was 3.7-5.0 $\mu g/m^3$ for each nitrosamine depending on the sample volume. An unknown substance thought to be a nitrosamine compound (not one of the seven) was detected in one of the samples collected in the coker unit. It eluted near N-nitrosodibutylamine (NDBA) and was quantitated (11 $\mu g/m^3$) relative to the NDBA reference standard.

TABLE IV-5. RESULTS OF NITROSAMINE AREA SAMPLES ($\mu g/m^3$)*

Sample Number	Process Unit	Sample Volume (m^3)	NDMA	NDEA	NDPA	NDBA	NPYR	NMOR	NPIP	Unknown
204	FCCU	0.811	<4.9	<4.9	<4.9	<4.9	<4.9	<4.9	<4.9	
224	Coker	1.073	<3.7	<3.7	<3.7	<3.7	<3.7	<3.7	<3.7	
228	Coker	0.794	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	**11
241	A.B.	1.003	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	
251	A.B.	1.075	<3.7	<3.7	<3.7	<3.7	<3.7	<3.7	<3.7	

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

*All seven nitrosamines were not detectable in any of the five (5) samples; values express detection limits.
**An unknown substance, possible a nitrosamine compound, that eluted near NDBA was detected. It was quantitated relative to the NDBA reference standard.

V. PHASE III

SAMPLING PROTOCOL

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 Sun Oil refinery. Sampling for airborne PAHs was conducted during the day shifts (0700-1500) on the second and third days of the survey in the four study process units. 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 V-1) was used with a portable MSA Model S pump. To investigate the influence of nonrespirable-size particles, a duplicate sampling setup was used with a cyclone preselector at each area sampling site at the FCCU, delayed coker, and asphalt blowing units. Personal samples were collected in the FCCU and coker only. A modified sampling device (Figure V-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 at the refinery's southwest boundary line was also collected. A total of 39 samples was collected over the 2 days.

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 27 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*/ Chyrsene*/Triphenylene
15. Benzo(e)pyrene*/ Benzo(a)pyrene*
16. Perylene
17. Dibenz(a,j)acridine*
18. Dibenz(a,i)carbazole*
19. Indeno(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.

B. Sampling Conditions

Weather conditions for the first sampling day (December 4) was clear skies with the temperature ranging from 50°F (10°C) in the morning (0800) to about 63°F (17°C) by early afternoon (1300). The relative humidity during this period ranged from 37% to 57% with the winds from the south and southwest at 2-7 mph.

Skies were again clear on December 5, with the temperature ranging from 58°F (14°C) at 0730, to 73°F (23°C) by 1300. Relative humidity ranged from 28% to 48% with winds from the south and southwest at 7-9 mph.

C. FCCU

Air Sampling

Two locations in the heavy fraction pump area near the fractionator (Figure V-3) were selected to collect the area samples at the FCCU. Location F-1, 4 feet above the spare slurry recycle pump and between the decanted oil and slurry recycle pumps, was sampled on December 4 during the day shift. Location F-2, also near the heavy fraction pumps and fractionator, was sampled on December 5.

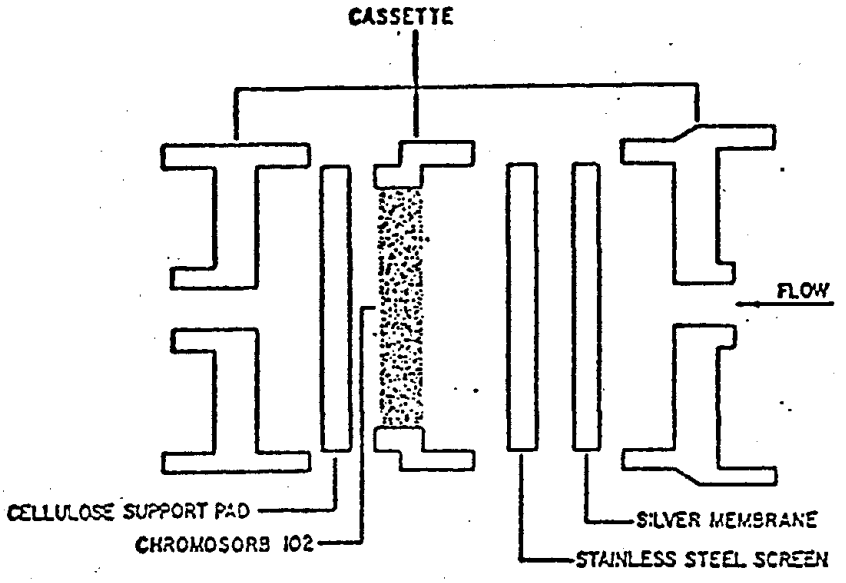


Figure V-1. Area Monitoring Device for PAHs

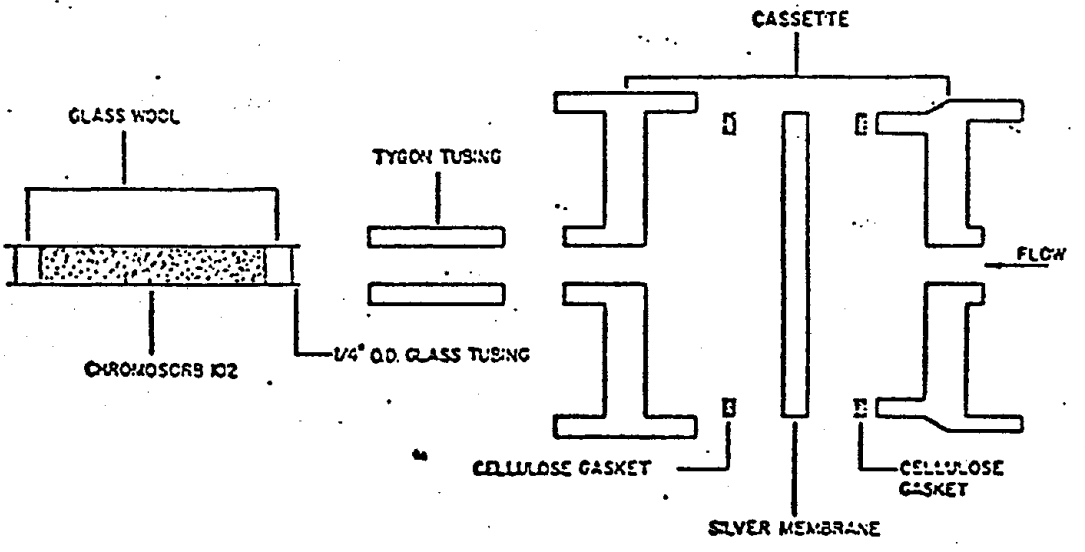


Figure V-2. Personal Monitoring Device for PAHs

The slurry recycle pump (steam-driven centrifugal pump) returns the fractionator tower bottoms, which include spent catalyst, back to the reactor. On both days the sampling units were repositioned during the sampling period to maintain a downwind location from the slurry recycle pump as the wind direction changed.

Personal Sampling

All six FCCU shift workers described in Chapter III were sampled during the day shifts on December 4 and 5.

D. Delayed Coker Unit

Area Sampling

Figure V-4 shows the two area sampling sites selected at the delayed coker unit. Location C-1, 2 yards south of the railroad tracks (and railcar during this shift) and downwind from the coke drums, was sampled on December 4. The sampling units were positioned about 4½ feet above ground level and just to the east of the coke tower elevator.

Location C-2 was just north and downwind of pump J-1A (steam-driven centrifugal pump), which moves feed from the fractionator bottom and surge tank to the furnace. This location was sampled on December 5. The cutting operation during both days lasted from about 0700 to 1130.

Personal Sampling

The two operational workers and the four coke cutters, described in Chapter III, were sampled during December 4 and 5.

E. Asphalt Blowing Unit

Locations A-1 and A-2 (Figure V-5) were sampled on December 4. Location A-1 was on the north side of the east blowing tower and just to the east of the asphalt pumps, which move the blown asphalt to storage tanks. Location A-2 was on the north side of the thermal oxidizer about 20 yards east of the blowing towers.

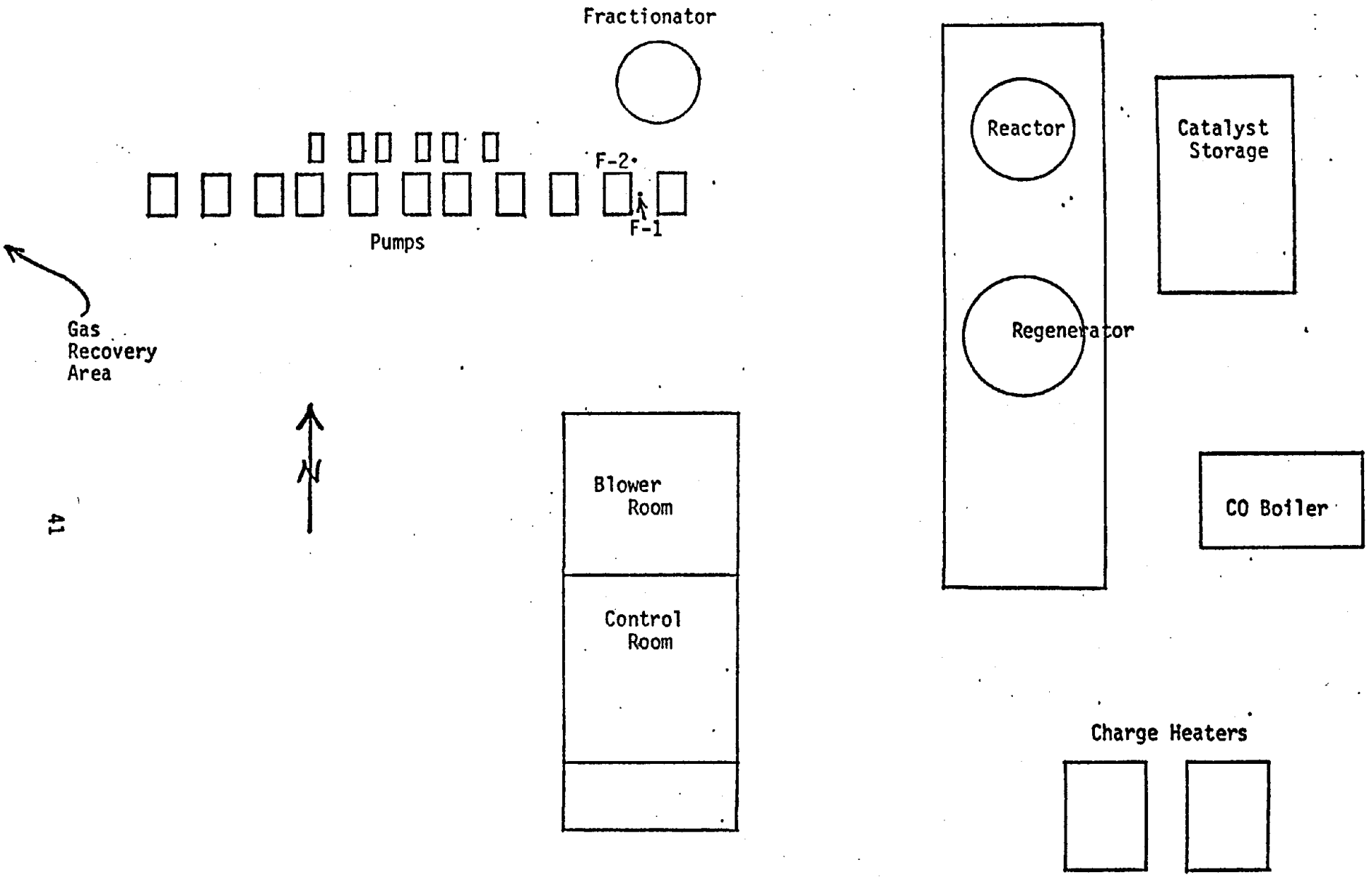


Figure V-3. FCCU Sampling Locations - Phase III

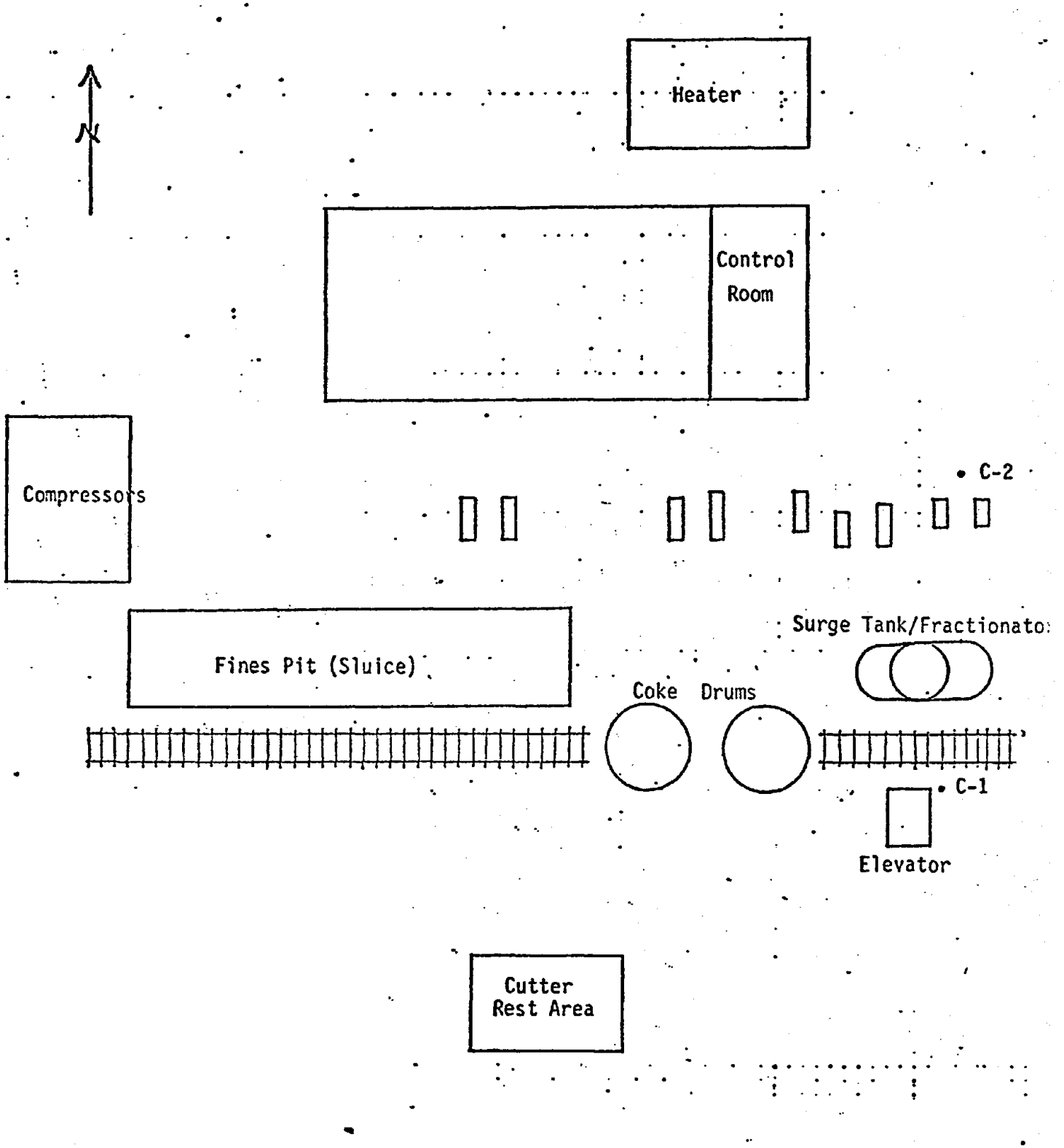


Figure V-4. Delayed Coker Sampling Locations - Phase III

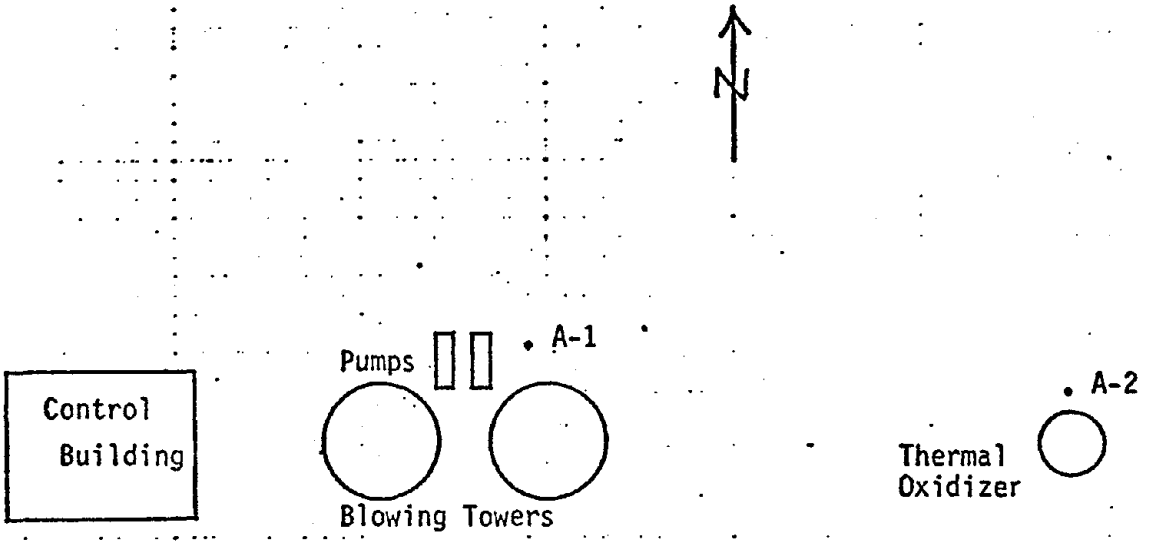


Figure V-5. Asphalt Blowing Unit Sampling Locations - Phase III

F. Deasphalting Unit

Both locations at the deasphalting unit (Figure V-6) were sampled on December 5. Location A-3 was on the east side of the unit between the deasphalting tower (E-31) and the asphalt stripper (E-42). The sampling unit was about 5 feet above ground and just to the north of pump J-32A which moves the asphalt from the stripper to storage tanks.

Location A-4 was in the central area of the unit on the south side of tower E-8, the asphalt flash tower and stripper. The sampling unit was about 5 feet above ground and 2 yards downwind of pump J-8, a vertical centrifugal pump (electric) that moves the asphalt from the stripper to storage tanks.

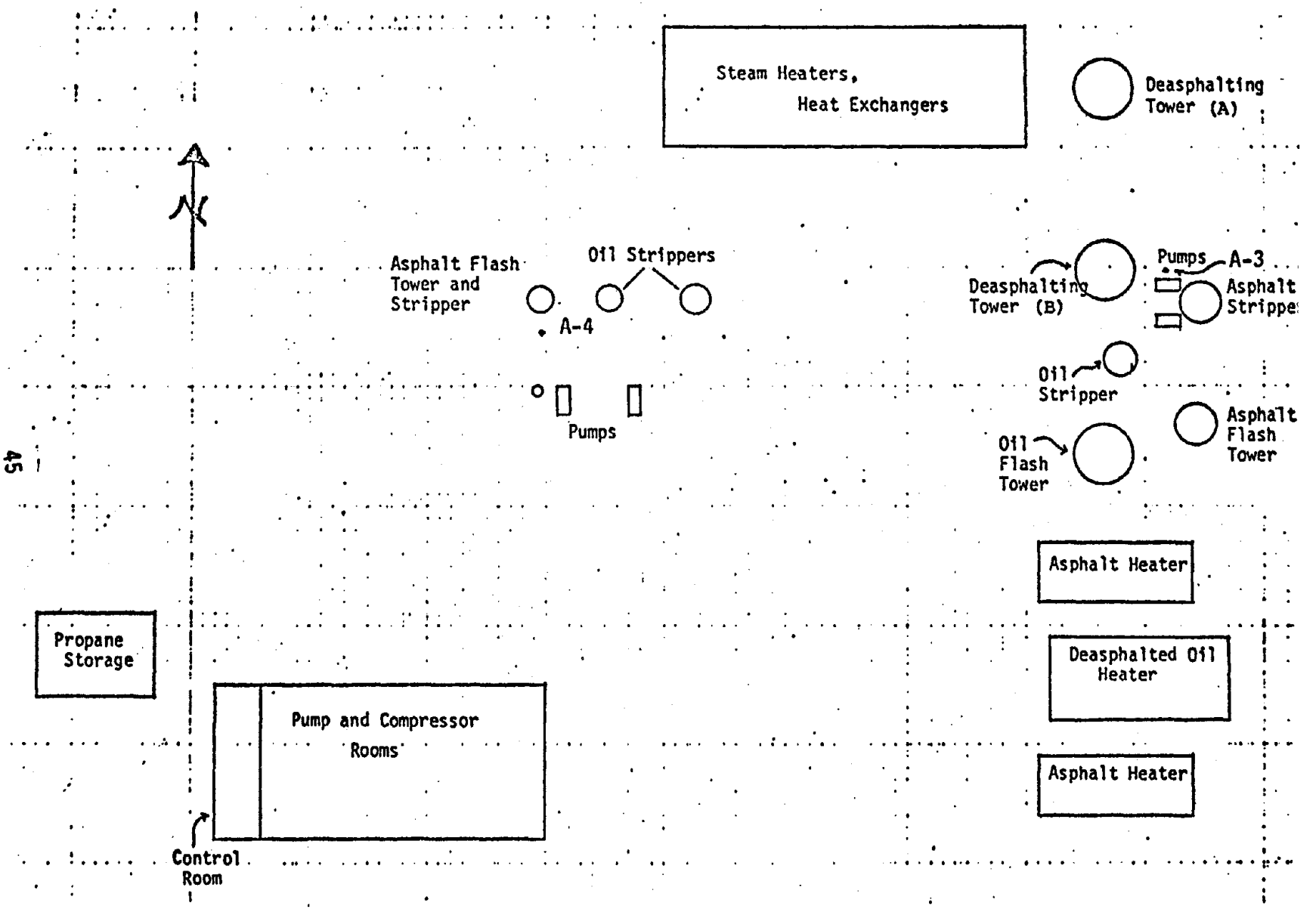


Figure V-6. Deasphalting Unit Sampling Locations - Phase III

RESULTS AND DISCUSSION

The complete results of the area and personal PAH samples collected at this Sun Oil refinery are presented in Tables V-1, V-2, and V-3. All 39 personal and area air samples analyzed from the four study process units had detectable quantitites of at least seven of the 23 PAHs (or groups of PAHs) for which the samples were tested. The cumulative PAH concentrations for individual samples ranged from 1.4 $\mu g/m^3$ for one area location in the deasphalting unit to as high as 70.8 $\mu g/m^3$ for a personal sample from one of the operators at the FCCU. The upwind boundary sample was about 1 $\mu g/m^3$.

In general the cumulative PAH concentrations were greater in the area and personal samples from the FCCU than from the delayed coker. The concentrations found in the area samples from the two asphalt processing units were less than those found in the other two study process units; this was expected, based on Phase II area sample results.

The distribution of individual PAHs by ring number was consistent in all samples. The 2-ring compounds were found in the highest concentrations and as the ring numbers increased the concentrations decreased. Only minimal amounts of the 5-, 6-, and 7-ring PAHs were found in the majority of the samples.

A. FCCU

The average (arithmetic mean) cumulative PAH concentration over the two shifts for the six FCCU workers was 34.9 $\mu g/m^3$ with the number of individual PAHs ranging from 11 to 23. Table V-4 shows that the four operators who spend a large portion of their shift outside (chief process operator and process operators) were exposed at higher concentrations than the two control room operators (35.9 versus 10.5 $\mu g/m^3$). These results, showing that the process operator having primary responsibility for the gas recovery area was exposed at the highest concentrations (43.1 $\mu g/m^3$) relative to the other two process operators, had not been expected due to the nature of the process streams in each of the unit areas.

TABLE V-I. PAH Analytical Results ($\mu g/m^3$) for Personal and Area Samples Collected at the FCCU**

	AREA (F-1)		AREA (F-2)		CHIEF OPERATOR		CONTROL ROOM OPERATOR		CONTROL ROOM OPERATOR		PROCESS OPERATOR A		PROCESS OPERATOR B		PROCESS OPERATOR C	
	12/4	12/4	12/5	12/5	12/4	12/5	12/4	12/5	12/4	12/5	12/4	12/5	12/4	12/5	12/4	12/5
	Total	Resp.	Total	Resp.												
Sample Vol. (ℓ)	780	794	794	780	944	927	834	934	968	925	941	880	923	916	890	930
Sample Time	0711-1427	0711-1427	0703-1419	0703-1419	0647-1421	0639-1407	0737-1422	0639-1406	0647-1423	0639-1406	0649-1419	0639-1406	0647-1413	0639-1406	0647-1410	0639-1406
NAPHTHALENE*	7.36	6.96	3.65	10.18	17.16	4.09	2.28	1.99	3.35	2.19	5.03	5.89	11.89	4.37	8.74	7.57
QUINOLINE	0.85	0.91	0.72	1.30	1.04	0.21	0.12	0.26	0.27	0.25	0.48	0.36	0.58	0.36	0.51	0.74
2-METHYLNAPHTHALENE	16.40	14.51	17.56	15.79	31.90	6.43	3.35	2.96	5.63	3.95	11.70	7.91	18.67	7.77	13.84	16.63
1-METHYLNAPHTHALENE	11.86	13.78	10.77	13.39	17.81	3.86	1.83	1.68	3.45	2.38	6.81	4.43	10.89	5.13	8.22	9.90
ACENAPHTHALENE	0.09	0.08	0.05	0.78	0.07	0.05	0.03	0.04	0.04	0.03	0.07	0.07	0.09	0.07	0.11	0.09
ACENAPHTHENE	1.09	1.02	1.34	1.70	0.74	0.46	0.22	0.26	0.27	0.25	0.51	0.42	0.46	0.49	0.41	0.80
FLUORENE	1.03	0.92	1.49	1.40	0.57	0.35	0.15	0.21	0.23	0.22	0.44	0.29	0.35	0.42	0.33	0.81
PHENANTHRENE† ANTHRACENE*	6.68	5.35	8.17	5.80	1.44	1.22	0.49	0.78	0.67	0.68	1.08	1.02	0.97	1.18	0.89	3.44
ACRIDINE	0.66	0.48	0.92	0.57	0.04	0.14	0.04	0.07	0.07	0.05	0.09	0.10	0.03	0.13	0.11	0.39
CARBAZOLE	0.32	0.24	0.52	0.23	—	0.08	0.02	0.03	0.02	--	0.02	0.05	--	0.06	0.03	0.18
FLUORANTHENE†	0.72	0.49	0.90	0.54	0.02	0.13	0.02	0.03	0.03	0.02	0.04	0.06	<0.01	0.07	0.04	0.24
PYRENE*	2.47	1.69	3.26	2.13	0.05	0.41	0.03	0.07	0.04	0.04	0.09	0.21	0.03	0.36	0.05	0.78
BENZOFLUORENE	0.50	0.36	0.72	0.44	—	0.10	—	<0.01	—	—	—	0.05	—	0.05	—	0.17
BENZ(a)ANTHRACENE† CHYRSENE† TRIPHENYLENE	0.60	0.29	0.63	0.29	—	0.09	—	0.01	0.01	—	0.01	0.06	—	<0.01	—	0.08
BENZO(e)PYRENE† BENZO(a)PYRENE*	—§	0.08	—	0.04	—	<0.01	—	0.02	—	—	—	<0.01	—	<0.01	—	—
PERYLENE	—	0.06	—	<0.01	—	<0.01	—	0.03	—	—	—	—	—	<0.01	—	—
DIBENZ(a,j)ACRIDINE*	—	0.08	—	<0.01	—	—	—	0.06	0.10	—	—	—	—	—	—	—
DIBENZ(a,i)CARBAZOLE*	—	0.19	—	—	—	0.04	<0.01	0.15	0.14	—	0.02	0.04	—	0.05	0.12	—
INDENO(1,2,3-cd)-PYRENE*	—	0.08	—	<0.01	—	—	—	0.03	0.04	—	—	—	—	—	—	—
DIBENZANTHRACENE*†	—	0.08	—	0.01	—	—	—	0.05	0.03	—	—	—	—	—	—	—
BENZO(g,h,i)PERYLENE	—	0.09	—	0.01	—	—	—	0.04	0.04	—	—	—	—	—	—	—
CORONENE	—	0.09	—	<0.10	—	—	—	<0.10	—	—	—	—	—	—	—	—
DIBENZPYRENE*†	—	—	—	—	—	—	—	0.18	—	—	—	—	—	—	—	—
TOTAL	50.63	47.83	50.70	54.60	70.84	17.66	8.58	8.95	14.43	10.06	26.39	21.59	43.96	21.59	44.29	41.82

* Suggested as having some cancer-causing potential.

** Blank values have been subtracted from data. Data have not been corrected for temperature and pressure variation; maximum deviation would be within ± 1% of actual values.

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

§ "--" designates compounds not detected.

TABLE V-2. PAH Analytical Results (μg/m³) for Personal and Area Samples Collected at Delayed Coker Unit**

	AREA (C-1)		AREA (C-2)		CHIEF PROCESS OPERATOR		K OPERATOR		Coke Cutters: HEAD CUTTER		DRILLER		1st HELPER		2nd HELPER	
	12/4	12/4	12/5	12/5	12/4	12/5	12/4	12/5	12/4	12/5	12/4	12/5	12/4	12/5	12/4	12/5
	Total	Resp.	Total	Resp.												
Sample Vol.(ℓ)	735	733	750	758	857	874	838	436	666	739	742	705	747	724	734	909
Sample Time	0713-1400	0714-1400	0703-1402	0708-1402	0702-1358	0656-1411	0706-1355	0655-1033	0655-1228	0645-1242	0646-1255	0648-1237	0644-1254	0637-1239	0648-1242	0643-1354
NAPHTHALENE *	2.04	1.98	3.62	3.95	4.02	12.90	19.27	15.62	1.75	0.76	8.72	4.99	3.76	2.93	4.10	6.16
QUINOLINE	0.31	0.17	0.81	0.95	0.26	0.52	0.45	0.85	0.24	0.15	0.42	0.22	0.28	0.48	0.52	0.42
2-METHYLNAPHTHALENE	2.34	1.70	5.69	5.64	4.14	13.02	19.05	22.61	2.61	2.16	12.03	5.15	4.71	4.78	6.26	4.50
1-METHYLNAPHTHALENE	1.17	0.99	3.55	3.08	2.21	10.81	10.21	12.09	1.44	1.01	4.85	2.15	2.26	2.05	3.11	2.12
ACENAPHTHALENE	0.04	0.04	0.05	0.05	0.02	0.05	0.07	0.07	0.04	0.03	0.08	0.03	0.06	0.05	0.07	0.04
ACENAPHTHENE	0.07	0.06	0.32	0.26	0.12	0.30	0.16	0.30	0.11	0.14	0.39	0.21	0.25	0.27	0.19	0.23
FLUORENE	0.10	0.07	0.25	0.20	0.11	0.17	0.13	0.26	0.14	0.17	0.61	0.34	0.34	0.44	0.21	0.35
PHENANTHRENE†/ ANTHRACENE*	0.51	0.24	0.37	0.38	0.19	0.20	0.20	0.43	0.25	0.42	1.20	0.84	0.76	1.42	0.36	1.06
ACRIDINE	0.11	0.03	0.07	0.06	0.02	0.03	0.02	0.08	0.03	0.04	0.07	0.07	0.12	0.12	0.04	0.14
CARBAZOLE	0.04	0.02	0.03	0.03	—	0.02	—	0.06	0.02	0.02	0.04	0.04	0.07	0.06	0.01	0.08
FLUORANTHENE	0.13	0.03	0.02	0.03	<0.01	<0.01	0.01	0.04	0.03	0.03	0.06	0.09	0.07	0.13	0.03	0.09
PYRENE *	0.53	0.10	0.07	0.06	0.01	0.01	0.01	0.07	0.05	0.09	0.16	0.19	0.16	0.32	0.07	0.20
BENZOFLUORENE	0.63	0.02	—	<0.01	—	—	—	—	—	0.02	0.04	0.04	0.04	0.09	0.02	0.05
BENZ(a)ANTHRACENE*/ CHYRSENE*/ TRIPHENYLENE	0.80	<0.01	—	0.02	—	<0.01	—	0.04	0.04	0.06	0.12	0.13	0.12	0.19	0.05	0.07
BENZO(e)PYRENE†/ BENZO(a)PYRENE *	1.40	—§	—	—	—	—	—	—	—	0.06	0.16	0.14	0.13	0.20	0.06	0.12
PERYLENE	0.24	—	—	—	—	—	—	—	—	—	—	0.01	0.04	—	—	0.04
DIBENZ(a,j)ACRIDINE *	0.72	—	—	—	—	—	—	—	0.07	—	—	0.01	0.22	—	—	0.11
DIBENZ(a,i)CARBAZOLE *	0.45	—	—	—	0.03	0.02	—	0.18	0.17	0.03	0.10	0.07	0.28	0.13	0.06	0.27
INDENO(1,2,3-cd)-PYRENE *	0.66	—	—	—	—	—	—	—	0.07	—	0.04	0.04	0.10	0.07	0.03	0.07
DIBENZANTHRACENE *†	0.89	—	—	—	—	—	—	—	0.07	0.02	0.09	0.06	0.15	0.13	0.05	0.09
BENZO(g,h,i)PERYLENE	1.10	—	—	—	—	—	—	—	0.11	0.03	0.12	0.09	0.14	0.15	0.07	0.09
CORONENE	0.26	—	—	—	—	—	—	—	0.18	—	—	—	0.10	—	—	—
DIBENZPYRENE *†	2.29	—	—	—	—	—	—	—	—	—	—	—	0.11	—	—	0.21
TOTAL	16.83	5.45	14.85	14.71	11.13	38.05	49.58	52.7	7.42	5.24	29.30	14.91	14.27	14.01	15.31	16.51

* Suggested as having some cancer-causing potential.

** Blank values have been subtracted from data. Data have not been corrected for temperature and pressure variation; maximum deviation would be within ± 1% of actual values.

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

TABLE V-3. PAH Analytical Results ($\mu g/m^3$) for Area Samples Collected at Asphalt Units and Upwind Location**

	ASPHALT BLOWING AREA (A-1)		ASPHALT BLOWING AREA (A-2)		DEASPHALTING AREA (A-3)		DEASPHALTING AREA (A-4)		UPWIND
	12/4	12/4	12/4	12/4	12/5		12/5		12/4
	Total	Resp.	Total	Resp.	Total		Total		
Sample Vol.(ℓ)	727	737	704	723	733		717		799
Sample Time	0724-1410	0727-1410	0738-1416	0740-1417	0740-1432		0745-1430		0754-1420
NAPHTHALENE*	1.13	1.50	0.37	2.21	0.12		2.68		0.28
QUINOLINE	0.05	0.06	0.08	0.09	0.12		0.35		0.10
2-METHYLNAPHTHALENE*	0.85	1.09	0.56	1.55	0.49		5.22		0.31
1-METHYLNAPHTHALENE	0.69	0.64	0.36	1.22	0.40		3.19		0.20
ACENAPHTHALENE	0.01	0.02	0.01	0.03	0.03		—		<0.01
ACENAPHTHENE	<0.01	0.02	0.01	0.03	0.04		0.14		0.03
FLUORENE	0.02	0.03	0.04	0.04	0.07		0.14		0.03
PHENANTHRENE*/ ANTHRACENE*	0.07	0.06	0.11	0.10	0.13		0.29		0.06
ACRIDINE	<0.01	0.02	--	0.02	0.03		--		0.01
CARBAZOLE	<0.01	0.01	--	<0.01	0.01		--		0.01
FLUORANTHENE	0.01	0.01	0.01	0.01	<0.01		--		<0.01
PYRENE *	0.02	0.02	<0.01	0.02	<0.01		—		<0.01
BENZOFLUORENE	--§	--	--	--	--		--		--
BENZ(a)ANTHRACENE*/ CHYRSENE*/ TRIPHENYLENE	<0.01	--	--	--	--		--		0.04
BENZO(e)PYRENE*/ BENZO(a)PYRENE *	--	--	--	--	--		--		--
PERYLENE	--	--	--	--	--		--		--
DIBENZ(a,j)ACRIDINE*	--	--	--	--	--		--		--
DIBENZ(a,i)CARBAZOLE*	0.04	0.05	--	--	--		--		--
INDENO(1,2,3-cd)-PYRENE*	--	--	--	--	--		--		--
DIBENZANTHRACENE *†	--	--	--	--	--		--		--
BENZO(g,h,i)PERYLENE	--	--	--	--	--		--		--
CORONENE	--	--	--	--	--		--		--
DIBENZPYRENE *†	--	--	--	--	--		--		--
TOTAL	2.89	3.53	1.55	5.32	1.44		12.01		1.07

* Suggested as having some cancer-causing potential.

** Blank values have been subtracted from data. Data have not been corrected for temperature and pressure variation; maximum deviation would be within ± 1% of actual values.

† Specific isomers not distinguishable by analtical method; reported value represents any one or combination of existing isomers.

§ "--" designates compounds not detected.

TABLE V-4. PERSONAL MONITORING RESULTS - FCCU UNIT

	No. of Samples	$\bar{X}$ (μg/m³)	No. of PAHs
Outside Operators	8	35.9	11-17
Chief Process Operator	2	44.3	11-17
Process Operator (gas recovery)	2	43.1	12-14
Process Operator (R/R)	2	24.0	14-16
Process Operator (roving)	2	32.2	11-17
Control Room Operators (2)	4	10.5	11-18

The results of the personal monitoring were quite consistent over the 2 days for four of the six workers. There was less than 31% difference between the duplicate samples collected for the two control room operators and two of the process operators. Both of the other operators were exposed at much higher concentrations during the first sampling day. 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 results of the two area samples collected without cyclones in the pump area near the fractionator were similar (50.6 μg/m³ and 14 PAHs identified, and 50.7 μg/m³ and 14 PAHs identified). For the duplicate sampling units with cyclones, the results were 47.8 μg/m³ (22 PAHs identified) and 54.6 μg/m³ (21 PAHs identified), respectively.

B. Delayed Coker Unit

Table V-5 gives a summary of the personal monitoring results for the six coke workers. These values are again average cumulative PAH concentrations for the two sampling days. Table V-5 shows that the two operational workers were exposed at higher concentrations than the four coke cutters; however, the coke cutters were exposed to a larger number of PAHs, especially the heavier compounds (Table V-2).

TABLE V-5. PERSONAL MONITORING RESULTS - COKER UNIT

	No. of Samples	$\bar{X}$ (μg/m³)	No. of PAHs
Operational	4	37.9	11-14
Chief Process Operator	2	24.6	12-14
Operator	2	51.1	11-14
Cutters	8	14.6	18-22
Head Cutter	2	6.3	19-20
Driller	2	22.1	19-21
Helpers (2)	4	15.0	19-22
Operational and Cutters	12	22.4	11-22

Of the two operational workers, the operator normally spends a much larger proportion of the shift outside in the production area. This is reflected in Table V-5 which shows the mean cumulative PAH concentration for the operator (51.1 μg/m³) versus the chief process operator (24.6 μg/m³). The head cutter was exposed at considerably lower concentrations over the 2 days compared to the other three cutters. This might be explained partially by the fact that there was an extra helper (a trainee) during both shifts, and as a result, the head cutter did not perform all of the duties he might have with a normal crew.

As in the FCCU, the results of personal monitoring were quite consistent over the 2 days for four of the six coke workers. There was less than 30% difference between the duplicate samples collected for the operator, the head cutter, and the two cutter helpers. For the chief process operator (CPO), the results were more than three times higher for the second sampling day. During this day the CPO spent at least 4 hours outside leading the shutdown and repair of a compressor, in addition to making his normal rounds. During the first day, the CPO spent about 1 hour outside, leaving the control room only to make the rounds of the unit. The results for the driller were almost twice as high on the first sampling day as on the second. The only differences noted were drum No. 1 was cut the first day and drum No. 2 the second day, and the driller's work station in the penthouse was different.

The two area samples taken in the coker unit without cyclones showed cumulative PAH concentrations of 16.8 $\mu g/m^3$ (23 PAHs identified) near the cutting operation and 14.9 $\mu g/m^3$ (12 PAHs identified) near the furnace charge pump. The duplicate area samples collected with cyclones showed cumulative concentrations of 5.5 $\mu g/m^3$ (14 PAHs identified) and 14.7 $\mu g/m^3$ (14 PAHs identified), respectively, for the same locations.

C. Asphalt Blowing Unit

The results of the two area samples collected without cyclones were 2.9 $\mu g/m^3$ (14 PAHs identified) at the blowing tower and asphalt pump, and 1.55 $\mu g/m^3$ (10 PAHs) at the thermal oxidizer. The duplicate area samples collected with cyclones were both higher, 3.5 $\mu g/m^3$ (13 PAHs) and 5.3 $\mu g/m^3$ (12 PAHs), respectively.

D. Deasphalting Unit

The results of the two area samples collected at this unit were 1.4 $\mu g/m^3$ (13 PAHs) at the first pump site, and 12.0 $\mu g/m^3$ (7 PAHs) at the second site near the asphalt pump and stripper. At this second site, there was a considerable amount of asphalt on and around the pump, indicating some type of leak. The only other difference noted was that the asphalt being processed was slightly different in composition at the two locations.

E. PAH Distribution

Table V-6 shows the percent distribution of PAHs found at the various units and upwind location by compound ring number. As the table indicates, in all locations, at least 87.0% of the PAHs found were the lighter molecular weight, 2-ring compounds. Naphthalene and its two methyl derivatives were the compounds found in the highest concentrations.

In the coker unit, one particular area air sample showed higher proportions of the heavier molecular weight PAHs than the other samples (Table V-2). This was the

total mass area sample collected downwind of the coke cutting operation (location C-1). The silver membrane filter was heavily loaded with black particulate matter (presumably coke) at the end of the sampling period. The duplicate sample collected with a cyclone preselector did not show nearly as much of the heavier molecular weight PAHs.

TABLE V-6. DISTRIBUTION (%) OF PAHs FOUND BY RING NUMBER

Ring No.	FCCU	Delayed Coker	Asphalt Blowing	Deasphalting	Upwind
2	87.0	90.8	92.8	95.0	86.0
3	9.5	4.5	5.4	5.0	10.3
4	3.2	1.8	0.9	0	3.7
5	0.2	1.9	0.9	0	0
6	0.1	0.9	0	0	0
7	0	0.1	0	0	0

VI. CONCLUSIONS

The Phase II results for this Sun 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 was 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 were 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).

The results of personal and area air samples collected during this Phase III survey clearly indicate that workers at the FCCU and delayed coker unit of this refinery are exposed to numerous PAHs, generally at low $\mu g/m^3$ concentrations. Only area samples were collected at the asphalt blowing and deasphalting units; however, the results of these area samples also indicate that possible worker exposure to detectable quantities of PAHs exists in these areas. In attempting to draw conclusions from this survey, one must keep in mind that the samples were collected over two work shifts during two 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 overall personal monitoring results from the FCCU and the delayed coker were similar. The mean cumulative PAH concentration over the two sampling shifts was 27.4 $\mu g/m^3$ for the six FCCU workers and 22.4 $\mu g/m^3$ for the six workers at the coker. The personal sampling results indicated that the outside workers were exposed at higher PAH concentrations than the inside workers. However, even those workers who spent the great majority of their shift within the control rooms were exposed at concentrations and a variety of different PAHs greater than anticipated. The results also indicated that coke cutters as a group were exposed at lower cumulative concentrations (14.6 $\mu g/m^3$) than the operational group at the coker unit (37.9 $\mu g/m^3$) and

outside operators at the FCCU (35.9 μg/m^3). However, the coke cutters were exposed at higher concentrations of the heavier molecular weight PAHs (i.e., 4- to 7-ring compounds) than these other worker groups. Only "sponge" or No. 2 grade coke was produced at this refinery.

The purpose of the limited area sampling at the FCCU and delayed coker 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. The results showed that many of the personal samples were just as high or higher than the area samples. This finding plus the levels found in the control rooms indicate that PAHs are not restricted to the areas around major emission sources but are widespread throughout many parts of these units. The area samples in the FCCU and coke unit indicate that the heavy fraction pump areas in both units are sources of PAH emissions. In the coke unit the downwind sample from the cutting operation also indicated, as expected, that the cutting operation generates airborne PAHs.

The number of PAHs or groups of PAHs identified in the majority of samples collected at this refinery was greater than expected based on Phase II area sample results. Most of the samples had detectable quantities of more than 10 PAHs and several samples had more than 20 PAHs identified. As expected from Phase II results, the great proportion of the PAHs identified were the lighter 2- and 3-ring compounds. However, the one area sample collected downwind of the cutting operation showed that higher molecular weight PAHs are contained in coke particulate.

Although it was not the original intention to compare the PAH results of Phases II and III, Table VI-1 shows there was a general consistency of the cumulative PAH concentrations between samples collected at comparable locations during the two surveys. This was especially true for samples collected at the FCCU (30.6 vs 50.7 μg/m^3) and the delayed coker unit (17.4 vs 15.8 μg/m^3). However, the distribution of PAHs was quite different; Phase III samples contained larger amounts of the heavier molecular weight PAHs. The Phase III samples collected at the two asphalt units were

considerably higher than those collected in Phase II; the upwind sample in Phase III was also higher.

TABLE VI-1. COMPARISON OF PAH AREA SAMPLES

Unit	PHASE II			PHASE III		
	No. of Samples	$\bar{X}$ (µg/m^3)	No. of PAHs	No. of Samples	$\bar{X}$ (µg/m^3)	No. of PAHs
FCCU	2	30.6	11-15	2	50.7	14
Coker	2	17.4	9-11	2	15.8	12-23
Asphalt Blower	1	0.4	4	1	2.9	14
Deasphalting	1	0.3	6	1	1.4	12
Upwind	1	0.2	5	1	1.1	13

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 results of the area samples collected side by side to compare the PAHs present in the total mass and respirable fraction (collected with a cyclone preselector) samples were inconclusive. As expected, both area locations sampled in the coker unit yielded higher PAH concentrations in the total mass sample. The one location downwind of the cutting operation showed considerable differences in the cumulative concentrations as well as much greater amounts of the heavier PAHs in the total mass sample. However, in both the FCCU and the asphalt blowing unit, one or both of the two locations sampled showed higher concentrations in the respirable fraction sample. The small number of side-by-side samples collected and the inconsistencies at the two process units make the results for this aspect of the survey inconclusive at this time.

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 II

Enviro Control, Inc.

Stan Futagaki	Senior Industrial Hygienist
Carl Bailey	Industrial Hygienist

NIOSH

Robert Herrick	Alternate Project Officer

Sun Oil

P.M. Reynolds	Manager of Tulsa Refinery
B.S. Sweatt	Manager, Employee and Plant Services
R.J. Murphy	Supervisor of Personnel and Safety
R.E. Eaton	Supervisor, Fire and Safety
R.A. Bui	Safety Engineer
E.T.W. Hall	Manager of Operations
W.L. Swander	Superintendent, Crude and Reforming
Jon Haas	Corporate Industrial Hygienist
John Verdi	Corporate Assistant Industrial Hygienist

Phase III

Enviro Control, Inc.

Stan Futagaki	Senior Industrial Hygienist
Edward Haggerty	Industrial Hygienist

NIOSH

Clinton Cox	Project Officer
Tom Bloom	Industrial Hygienist

Sun Oil

R.J. Murphy	Supervisor of Personnel and Safety
R.E. Eaton	Supervisor, Fire and Safety
R.A. Bui	Safety Engineer