PHASE III SURVEY REPORT #1

WORKER EXPOSURE TO POLYAROMATIC HYDROCARBONS AT SELECTED PETROLEUM REFINERY PROCESS UNITS

SURVEY LOCATION:

CHAMPLIN PETROLEUM REFINERY

ENID, OKLAHOMA

SURVEY DATES:

30 NOVEMBER - 1 DECEMBER 1979

REPORT DATE:

JUNE 1980

DISCLAIMER

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ABSTRACT

This industrial hygiene survey of a petroleum refinery is one of nine performed during Phase III of a NIOSH-sponsored study characterizing worker exposure to polyaromatic hydrocarbons (PAHs) in three different types of process units. Personal and area air samples were collected in the fluid catalytic cracker and delayed coker units and area samples only in the asphalt processing 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 35 of the personal and area air samples had detectable quantities of at least five PAHs or groups of PAHs with the cumulative PAH concentration for individual samples ranging from less than 1 μg/m^3 for one area location in the coker unit to as high as 150 μg/m^3 for a personal sample from one of the coke workers. The two upwind boundary samples were each less than 1 μg/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, the delayed coker, and the asphalt processing unit.

- Phase II: An attempt was made 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.

Phase III is currently in progress. The Champlin Petroleum refinery at Enid, Oklahoma was the first refinery visited as part of Phase III and this report presents the information and air-sampling data for PAHs collected during this survey.

The Phase III industrial hygiene survey of the Champlin refinery was conducted over a period of three days, from November 29 to December 1, 1979. The first day was devoted to an opening conference and a walk-through of the study process units; the personal and area air-sampling program was carried out on the second and third days. Initial contact for this visit was made through the corporate Director of Safety and Loss Control. All subsequent arrangements were made through the refinery Safety Engineer.

The opening conference was held with representatives from the refinery, the refinery corporate office, NIOSH, and Enviro (list of attendees in Appendix). The two representatives from Enviro and the Project Officer from NIOSH described the project, the status, and the specific objectives of the survey. A tentative schedule was agreed upon for the three days. A similar conference was held with two representatives of the Oil, Chemical, and Atomic Workers International Union (OCAW) employed at the refinery. After the meetings, the survey team conducted a walk-through of the three process units to be sampled. At the fluid catalytic cracker (FCCU) and the delayed coker, where personal monitoring was scheduled, the Enviro industrial hygienists explained the sampling procedures to the employees.

On the day shift of the second day, area and personal sampling was conducted in the FCCU and delayed coker unit. Only area samples were collected in the asphalt processing unit. On the day shift of the third day, the sampling was repeated in the FCCU and asphalt unit. Because of the coke cutting schedule during the third day, this unit was sampled during the evening shift.

II. DESCRIPTION OF REFINERY

This Champlin refinery is located on the outskirts of Enid in northwestern Oklahoma. With its crude capacity of 53,800 bbl/day, it is classified as a "medium-size" refinery for the purposes of the study. Since the oil company that owns this refinery and two others (one in Texas and one in California) is not one of the largest 15 companies in terms of crude capacity, the company is considered a "nonmajor" oil company. The significance of categorizing this refinery by these criteria is explained in the Phase II report.

This refinery originated in 1916 as a 1,000 bbl/day crude oil skimming plant. Currently spread out over 608 acres, it processes over 50,000 barrels of crude a day and produces a full line of petroleum products which includes:

- liquid petroleum gas (propane, butane)
- jet fuel
- gasolines
- Diesel fuel
- #2, #6 fuel oils
- lube oils
- coke
- asphalt

The domestic crude refined here is categorized as a "sweet" (0.23% sulfur by weight), "mixed base" (containing both paraffins and naphthenes) crude with an API Gravity Index of 39.5. Approximately 32,000 bbl/day come from Oklahoma and 21,500 bbl/day come from west Texas. Most of the crude is received by pipeline; a small percentage is received by tank trucks.

This refinery is capable of shipping gasolines, fuel oils, and Diesel fuels by a highly automated pipeline that goes north to Rock Rapids, Iowa, and south to Oklahoma City. Products are also shipped by trucks and railroad cars.

The major process units at the Champlin refinery include:

- two crude distillation units
- two vacuum distillation units
- duo-sol lube unit
- delayed coker
- asphalt blower
- unifiner
- catalytic reformer
- catalytic isomerization unit
- FCCU
- HF alkylation unit

Almost every major process unit has its own control room. Figure II-1 shows a rough refinery plot plan of the major units. South of the process units, there is also a lubricant packaging plant where quart, five-gallon, and fifty-gallon containers are filled.

There are approximately 270 hourly employees that belong to the union (OCAW) and an additional 20 that are salaried (supervisory 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.

The safety and health staff at this refinery includes the manager of safety, a safety engineer, two fire and safety helpers, and an occupational nurse. All are under the direct supervision of the refinery superintendent. The nurse is on the premises full time during the day shift; a majority of the supervisors and foremen are trained in first aid and cardio-pulmonary resuscitation. The dispensary and treatment room is fully equipped to handle first-aid situations and various routine examinations. All of the production workers are given preplacement medical examinations, although a set schedule for periodic examinations has not yet been established. A physician in town is under contract to the company to handle examinations and other medical situations.

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 routine cleanup is performed by the day-shift unit operators. Any necessary equipment or structure repair is also promptly carried out by the unit operators or in-house maintenance crews.

Routine industrial hygiene sampling is not performed at this refinery. Sampling has been carried out on a spot basis for benzene, heptane, hexane, hydrogen sulfide, and sulfur dioxide.

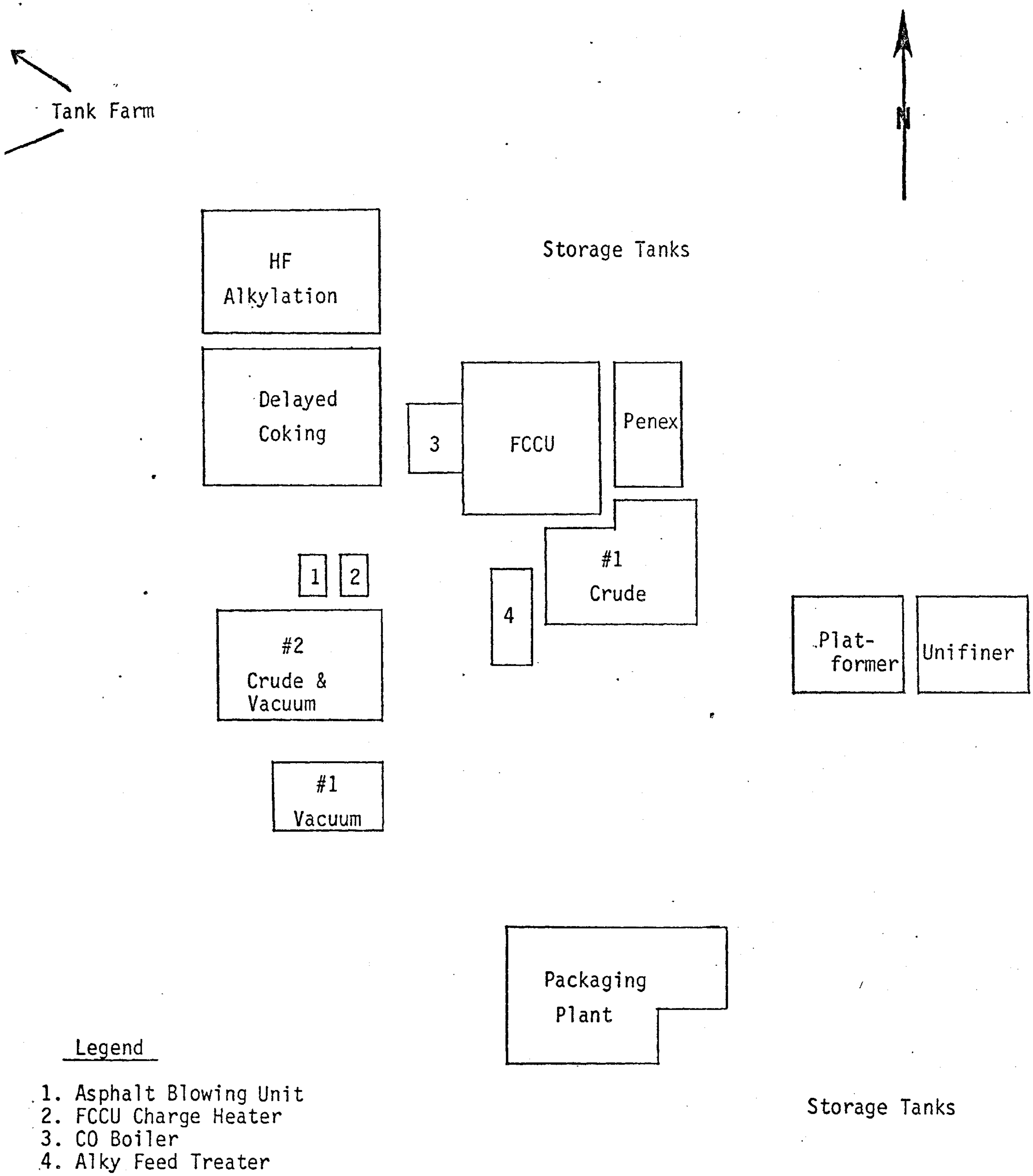

Figure II-1. Refinery Production Area

III. STUDY PROCESS UNITS

FLUID CATALYTIC CRACKING UNIT (FCCU)

A. Unit and Process Description

The FCCU is located in the middle of the main production area (Figure II-1) about 200 feet east of the delayed coker unit and just to the northeast of the No. 1 crude unit. The reactor/regenerator structure is a stacked type with the regenerator on top. The total height of the structure is 185 feet. The unit was designed and installed in the early 1950s. A major modification in the riser size was made about 1962 that extended the production capacity to the present-day figure of about 20,000 bbl/day.

The unit covers an area of about 200 x 200 feet with the CO boiler located just to the east of this area (Figure III-1). The FCCU charge heater is about 100 feet to the southwest of the unit across the main road of the refinery. The main portion of the FCCU is laid out into three areas:

1) The reactor/regenerator (R/R) structure, the fractionator tower, and the various pumps are located in the center of the unit running west to east.

2) The gas recovery area is situated just to the north of these structures. Gas recovery includes the primary absorber, gas stripper, secondary absorber, and debutanizer towers.

3) Just to the south of the R/R structure are the fresh and regenerated catalyst hoppers, the pump room, and the control house. A compressor building is located just south of the pump room.

The fresh feed for the FCCU comes from the crude units (atmospheric gas oil) and the vacuum units (mostly light and heavy vacuum gas oils). The feed is preheated to a suitable temperature by a gas-fired furnace.

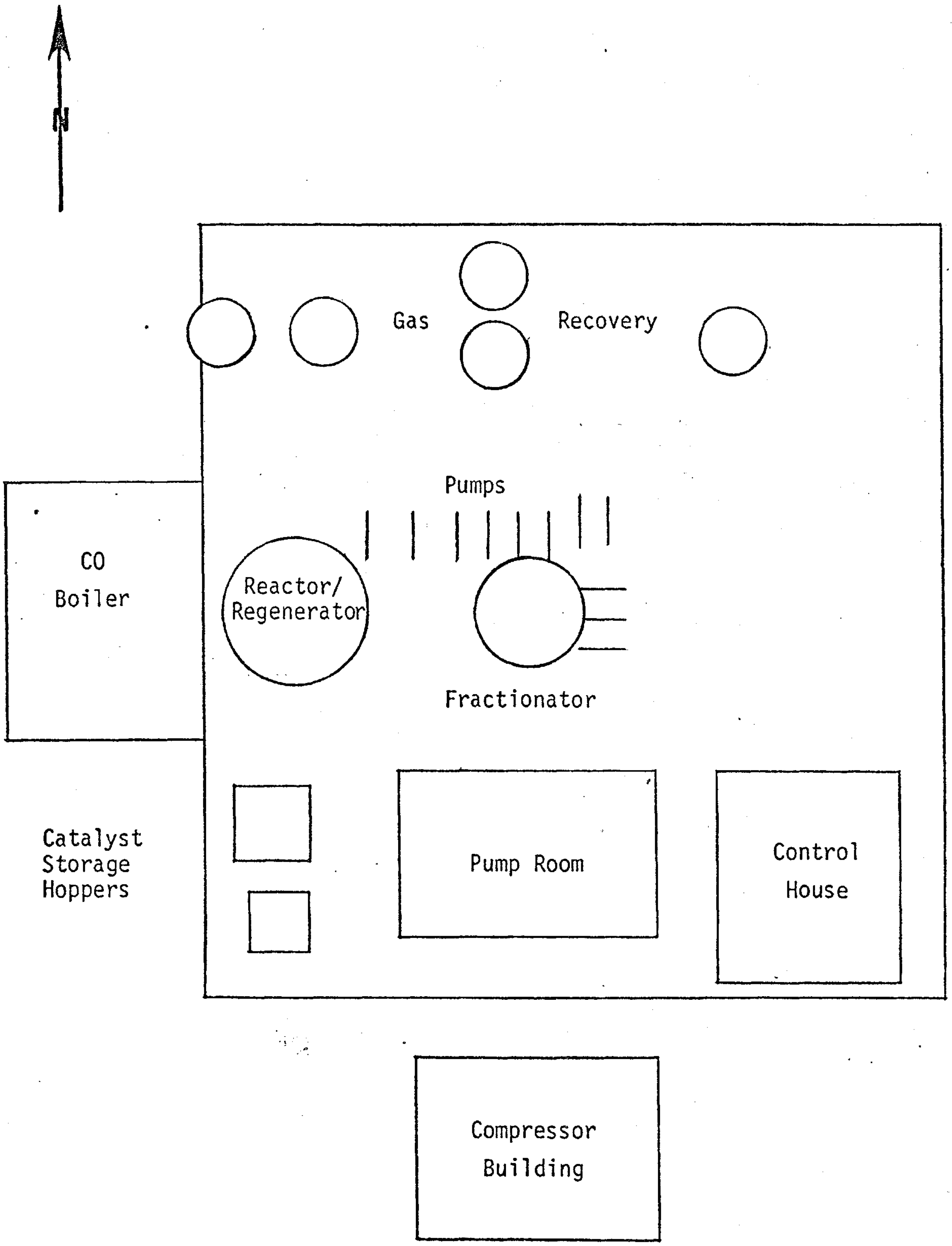

Figure III-1. FCCU

This fresh feed plus heavy gas oil recycled from the fractionator are injected into the reactor where catalytic cracking is initiated as the hot oil feed contacts the catalyst. The catalyst used at this refinery is an alumina-like synthetic zeolite common in other FCCUs studied in this project. The product vapors and the catalyst are separated in the single feed riser line and the reactor itself. The hydrocarbons are taken to the fractionator tower where the various products are separated. The catalyst is stripped of any remaining oil with steam and delivered to the regenerator where the spent catalyst is reactivated by oxidizing the accumulated carbon at a temperature of about 1200^{o}F. The flue gas from the regenerator goes to the CO boiler where it is burned before being released to the atmosphere. The regenerated catalyst is stripped of any absorbed oxygen with steam before being recirculated back to the reactor. The continuous circulation of the fluidized catalyst is an important means of heat transfer between the reactor and regenerator.

The main products from the fractionator are:

- butane
- propane
- heavy cat gasoline
- light cycle oil
- decant oil

B. Workforce

There are normally five workers assigned to the FCCU full time during each shift. In addition, there is an assistant supervisor on duty from 0800 to 1700 each day who spends about 70% of his time on this unit. Following is a brief description of the duties of the five full-time shift personnel.

- shift foreman: Supervises the overall unit operations paying particular attention to any operational difficulties as well as any specific fire or safety hazards, such as gas leaks. He spends about a third of his time outside the control room directing the helpers.

- control room operator: Spends essentially 100 percent of his shift inside, monitoring and logging in the various meters and charts on the control board. He works closely with the shift foreman, as well as with the helpers and operator.

- CO boiler operator: This outside operator has primary responsiblity for the CO boiler. His duties include collecting water samples and adding chemicals at the FCCU cooling tower and the CO boiler unit, making rounds every two hours (30 min/round) to check meters and gauges, and greasing and lubing equipment, such as pumps (daily or weekly schedule).

- operator and helper: These are two operators that perform the routine outside duties for the main section of the FCCU; their job duties and responsibilities are essentially the same. Periodically they take meter and gauge readings, make visual inspections, gauge tanks, collect process samples once per shift, monitor uptake of chemical additives, keep pumps oiled, and maintain the unit by general housekeeping.

C. Exposure Control Measures

The primary exposure control measure used at this FCCU 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 during sampling of the various streams, during maintenance and housekeeping activities, from fugitive emissions, and from the regenerator flue gas.

The use of sample bombs for collecting process stream samples is a means of minimizing exposure; these bombs are used for collecting at least some of the stream samples at this unit. The sample bomb is placed in an auxiliary process line and the stream is diverted through this line, filling the vessel. The valves at each end of the bomb are closed and the bomb can be removed with minimum exposure to the collector. Samples are also collected using the spigot-and-bottle method which is not as effective in minimizing exposure.

Exposure during routine maintenance is difficult to minimize. The ground level of the unit is constructed of concrete with an efficient sewer system that simplifies cleanup procedures. The refinery has its own craft maintenance crews (e.g., pipefitters, electricians) that provide preventive and repair services. Hard hats, safety glasses, and neoprene gloves are routinely worn, with safety or slick suits available. Coveralls are not provided and are not normally worn. Disposable ear plugs are used when in the enclosed compressor room. 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 decant oil pumps are located very close together around the base of the fractionator tower. This is an area where PAHs concentrations might be elevated. The control house, which is air conditioned but not under positive-pressure ventilation, is normally not directly downwind of the R/R or heavy fraction pumps.

The flue gas from the regenerator is burned in the CO boiler with an auxiliary fuel. The heat produced here is used to generate steam. The CO boiler not only removes carbon monoxide from the flue gas, but many other 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 just south of the HF alkylation unit; north of the No.2 crude, vacuum, and asphalt blowing units; and west of the FCCU and CO boiler. The unit has two 75-foot coke drums with a daily production capacity of about 200 tons.

The unit, which is about 10 years old, is spread over an area of about 200 x 200 feet (Figure III-2). The ground level of the entire unit is constructed of concrete. The control building is located in the central area of the unit and houses the locker and shower facilities in addition to the control board room. Just north of the control building is the coke tower (an open, multi-level structure that includes the two drums and penthouse at the top) with the trough and loading area on the other side. The coke that has been cut is moved from the trough to the loading area by a Diesel-powered crane.

The gas-fired charge furnace is located about 15 yards to the east of the control building with the fractionator in between. The gas recovery structures and flare are located to the west of the control building and coke tower.

There are two types of coke produced at this refinery, a #1 grade coke referred to as "needle" coke and the more commonly produced #2 grade coke or "sponge" coke. The charge stock is decant oil from the FCCU for needle coke and the residual from the vacuum units for sponge coke. Needle coke is a higher-quality coke that is much harder and denser than the sponge type.

The residual from the vacuum units or the decant oil is pumped from storage tanks and regulated by a charge motor valve to the convection portion of the gas-fired box heater. The heated charge then goes to the fractionator tower where the light ends are flashed off. The bottoms from the fractionator are then pumped to the radiant side of the furnace. At this point the charge for sponge coke is heated to about 900^{o}F; the charge for needle coke is heated about 45^{o}F higher. The charge then goes to one of the two coking drums. Each drum has a 40-hour cycle with coke formation lasting

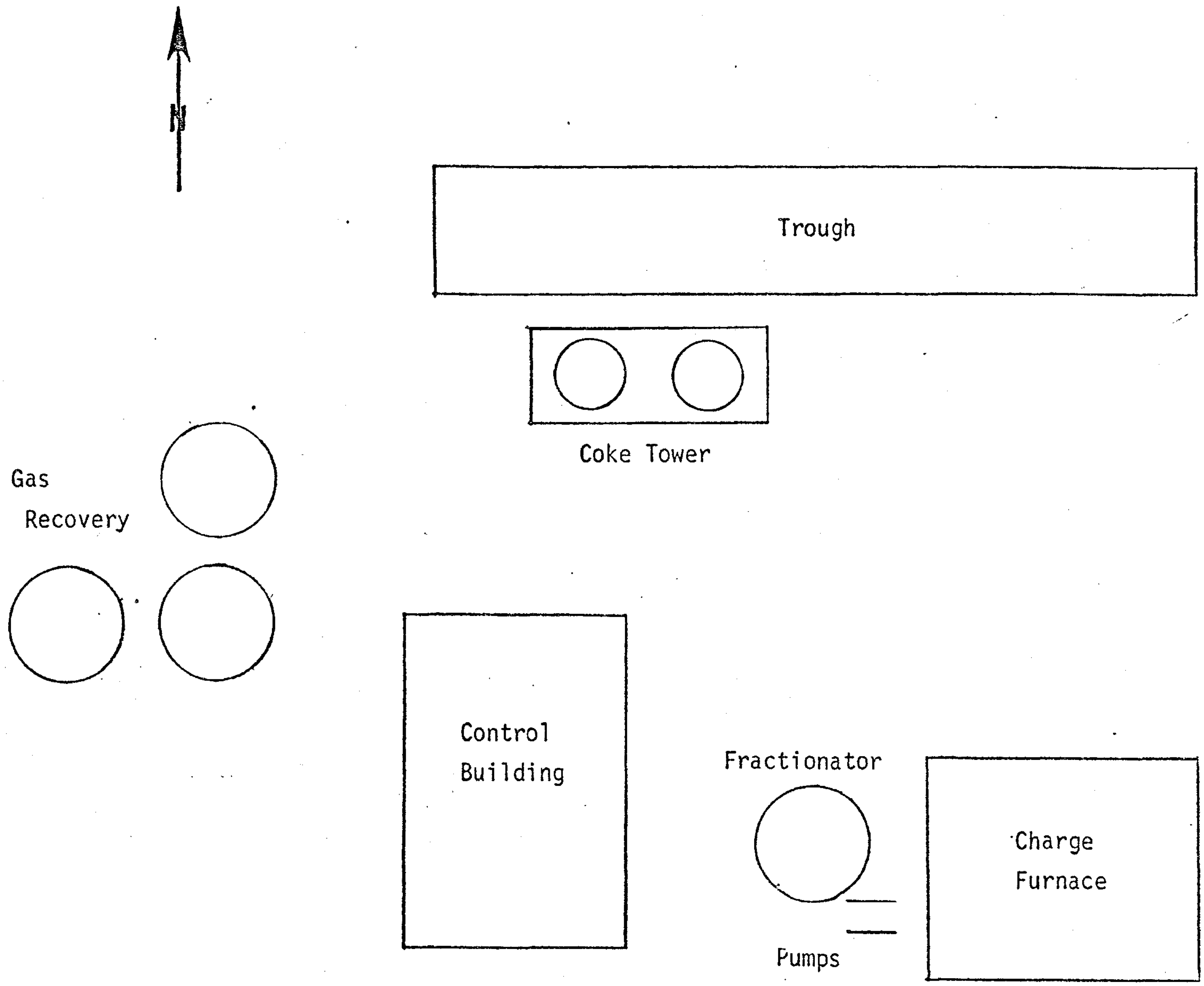

Figure III-2. Delayed Coker Unit

about 20 hours. Since the drums work as a pair, cutting of one drum occurs every 20 hours. 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. Products from this unit besides coke include: gas oil, gasoline, naptha, propane, and butane.

The complete cycle of each drum from drum heating to cutting is 40 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 the coke is cut from the top with a high-pressure hydraulic bit. The coke falls down a chute into a trough from which it is moved to a loading area by a Diesel-powered crane. Trucks are used to transport the coke. The drilling lasts from 2 to 4 hours, depending on the type of coke being cut. Since needle coke is much harder, its cutting operation lasts longer.

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 three-man operations group works the normal 8-hour shift; following is a brief description of their job activities.

- operator: Is in charge of the normal unit operations. He spends most of his time inside the control room where he can easily monitor operations. He occasionally leaves the control room to assist one of the others or to lead a more difficult task, such as pump repair.
- first helper: His main responsibilities are to monitor the control board, make entries into the daily log sheet, and make

the necessary process control adjustments. He spends a majority of his shift inside. He occasionally makes process checks in the production area.

- second helper: Performs most of the routine outside tasks spending a total of 2 to 4 hours a shift in the production area. About every 2 hours he makes routine rounds checking temperature, pressure, and flow rate gauges, making visual inspection of equipment and processes, and switching valves. He also does most of the daytime cleanup in the production area and draws four water samples once a shift. The samples are sent to the laboratory for routine testing.

The coke-cutting group is made up of the driller, the first and second helpers, and the crane operator. This group works independently of the operations crew. They come in about 30 minutes before a drum is scheduled to be cut, work until the cutting and cleanup is finished, shower, and leave. This usually takes 5 to 6 hours. The total work group consists of five to six drillers and helpers, and two crane operators.

- driller: Spends about 15 minutes opening the top of the drum and 15 minutes opening the bottom. He then goes back to the top to the "penthouse" where he controls the drilling operation. He usually stays there during the entire cutting operation except for breaks. He helps to close the drum when the operation is completed.

- first helper: Helps to open the top and the bottom of the drum, and to get the chute in place. While the cutting is being done, he cleans up loose coke with a water hose, and lubricates and prepares all fittings for reassembly.

- second helper: Duties similar to first helper.

- crane operator: Spends most of the shift in the crane cab moving the coke from the trough to the adjacent truck-loading area. The crane cab is usually open in front. The crane is normally upwind of the cutting operation and trough.

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, the helpers must clean and lubricate the fittings, and the crane operator must move the coke out of the trough. Basically the coke-cutting operations at this refinery were similar to those observed at other refineries; however, there were several key points observed.

The opening of the top and bottom of the drum was done very efficiently and quickly. The three cutters (the driller and two helpers) worked as a team to complete both openings in about 30 minutes. After the bottom is dropped, a chute extender is lifted up from the floor platform to the bottom of the drum and secured with several bolts. This forms a closed system on this level where the helpers spend a good part of their time during the operation.

The penthouse on the top level and the bottom of the drum on the second level were fairly open areas minimizing accumulation of vapors. In the penthouse, the driller was seated so that he was normally upwind of the top of the drum. The whole cutting operation at this refinery was relatively clean, requiring a minimum of cleanup, usually performed by hosing down the area with water.

All workers wore hard hats, safety glasses, and gloves on this unit. Neither the cutters nor the operational crew wore coveralls but the cutters did normally change into a set of work clothes in the locker room and showered or washed up at the end of their shift. The operations crew ate in the control room while the cutters did not stop to eat. There were no routine operations that required the use of respirators; however, air-purifying and self-contained-breathing-air respirators were available.

The air-conditioned control room was not under positive-pressure ventilation but was normally upwind of the coke tower, furnace, and furnace charge pump. This refinery is considering changing to one main control room in the future.

The steam that is used to cool the drums down is normally sent through a water scrubbing system before it is vented to the atmosphere. There is a flare on the west side of the unit that is available for turnarounds or any other conditions that might require it.

ASPHALT PROCESSING UNIT

A. Unit and Process Description

The asphalt-blowing unit is a small (approximately 80 by 40 feet) and a relatively simple unit in terms of process flow and equipment. The main structures are two towers located side by side, one being the blowing still and the other the water scrubber for the still vent gases. The unit is located between the No. 2 crude and vacuum units, and the delayed coker unit. The gas-fired FCCU charge heater is next to the unit just to the east. This unit does not have its own control room; its control board is part of the No. 2 crude unit control room located about 75 feet from the blowing tower.

During normal operations, part of the bottoms from the No. 2 vacuum tower is pumped to the blow still. Here a stream of air is blown through the tower oxidizing the heavy residue material. The vent gas is then sent through the adjacent water scrubber and burned in the FCCU charge heater. The blowing process increases the hardness and melting temperature of the asphalt product. After the desired penetration grade is achieved, the asphalt is pumped to storage tanks. The average production of blown asphalt is 500 bbl/day; however, the actual blowing process was not in operation during the survey. The asphalt from the vacuum tower was being pumped through the blow still to the storage tanks without being blown. This is normal procedure when the asphalt tanks are full or if the market does not demand additional asphalt production.

B. Workforce

No workers are assigned full time to the asphalt blowing unit. Two outside operators who have primary responsibility on the No. 2 crude unit handle the routine operations for this unit.

IV. SAMPLING PROGRAM

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 Champlin refinery. Sampling for airborne PAHs was conducted on the second and third days of the survey in the three 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 IV-1) was used with a portable MSA high-flow pump. To investigate the influence of nonrespirable-size particles, a duplicate sampling setup was used with a cyclone preselector at each area sampling site. Personal samples were collected in the FCCU and coker unit only. A modified sampling device (Figure IV-2) was used for personal monitoring for PAHs. The chromosorb was packed in a glass tube following the cassette rather than in the cassette itself. Upwind samples at the refinery boundary line were also collected. A total of 37 samples was collected over the two days.

The samples were analyzed by gas chromatography/mass spectrometry which allowed the quantitative analysis of the following 23 individual or groups of PAHs and azo-heterocyclic 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(e)fluorene
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. 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). Although specific isomers of 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.

SAMPLING CONDITIONS

Weather conditions for the first sampling day (November 30) were clear skies with the temperature ranging from 30°F in the early morning (0600) to about 50°F by early afternoon (1330). The relative humidity during this period ranged from 12% to 40% with the winds from the west and northwest at 4-7 mph, gusting to about 13 mph.

Skies were clear on December 1, with the temperature ranging from 32°F at 0730, up to 45°F by 1630, and down to 33°F by 1905. Relative humidity ranged from 52 percent to 60 percent with winds from the north and northwest at 3-6 mph.

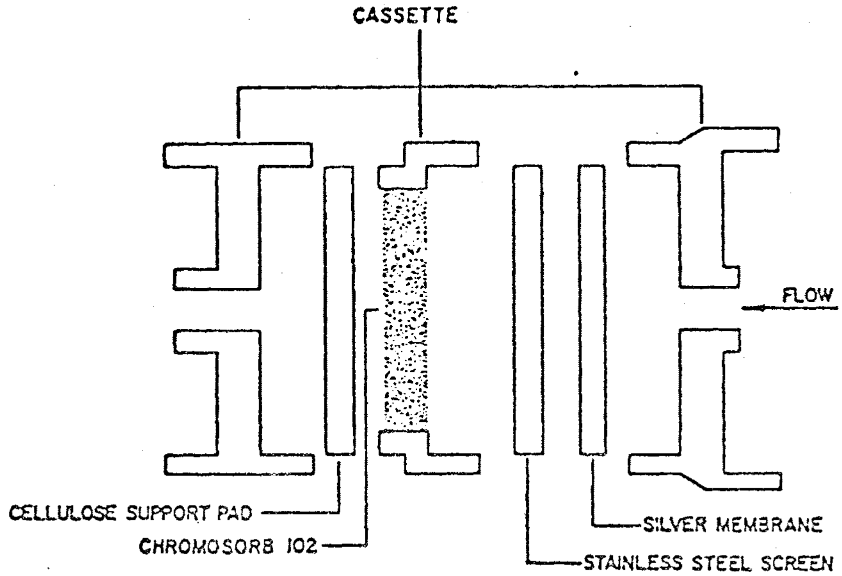

Figure IV-1. Area Monitoring Device for PAHs

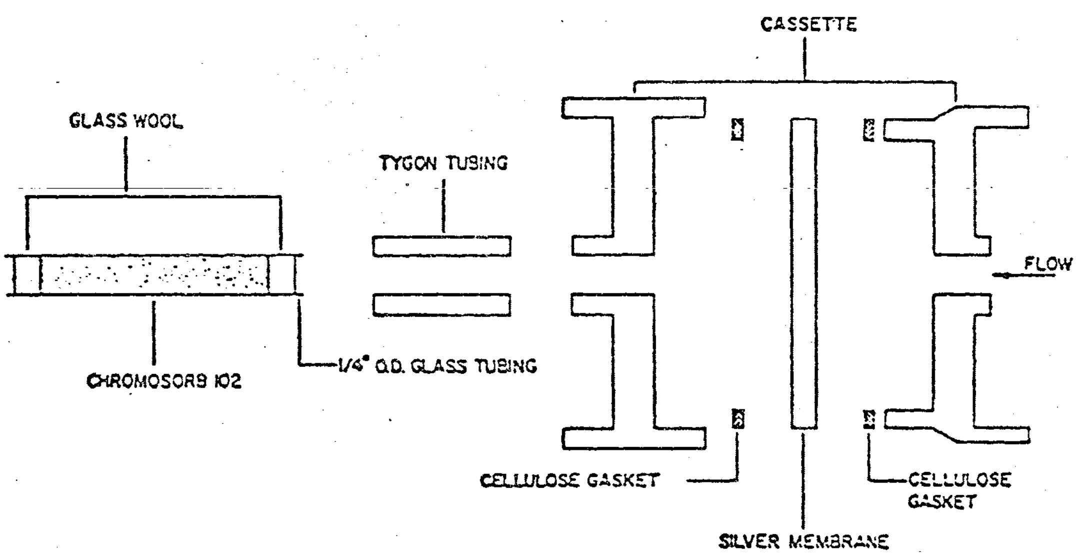

Figure IV-2. Personal Monitoring Device for PAHs

FCCU

A. Area Sampling

Two locations in the pump area near the fractionator (Figure IV-3) were selected to collect the area samples in the FCCU. Location F-1, about 5 feet above ground level on slurry recycle pump J-4A was sampled on November 30, during the day shift. This centrifugal pump returns the fractionator tower bottoms, which include spent catalyst, back to the reactor. There were several heavy fraction pumps in the close vicinity.

Location F-2 was sampled during the day shift on December 1. The sampling unit was situated about 3½ feet above ground level on decant oil pump J-5. This was 15 to 20 feet downwind of the slurry recycle.

B. Personal Sampling

An attempt was made to monitor all five shift workers during the day shifts on November 30 and December 1. However, the operator was uncomfortable wearing the portable pump and only a partial sample on the first day was collected for this particular worker.

DELAYED COKER UNIT

A. Area Sampling

Figure IV-4 shows the two area sampling sites selected in the delayed coker unit. Location C-1, 15 yards east and downwind of drum B, was sampled during the day shift on November 30. The samples were collected 5 feet above ground level, 3 yards south of the trough, 20 yards south of the coke loading operation, and 40 yards west of the CO boiler.

Location C-2, located 3 feet downwind of pump 113A, which sends the bottoms from the fractionator to the radiant side of the furnace, was sampled during the evening shift on December 1. The cutting operation during the first day lasted from 0600 to 1000 and on the second day from 1800 to 2100.

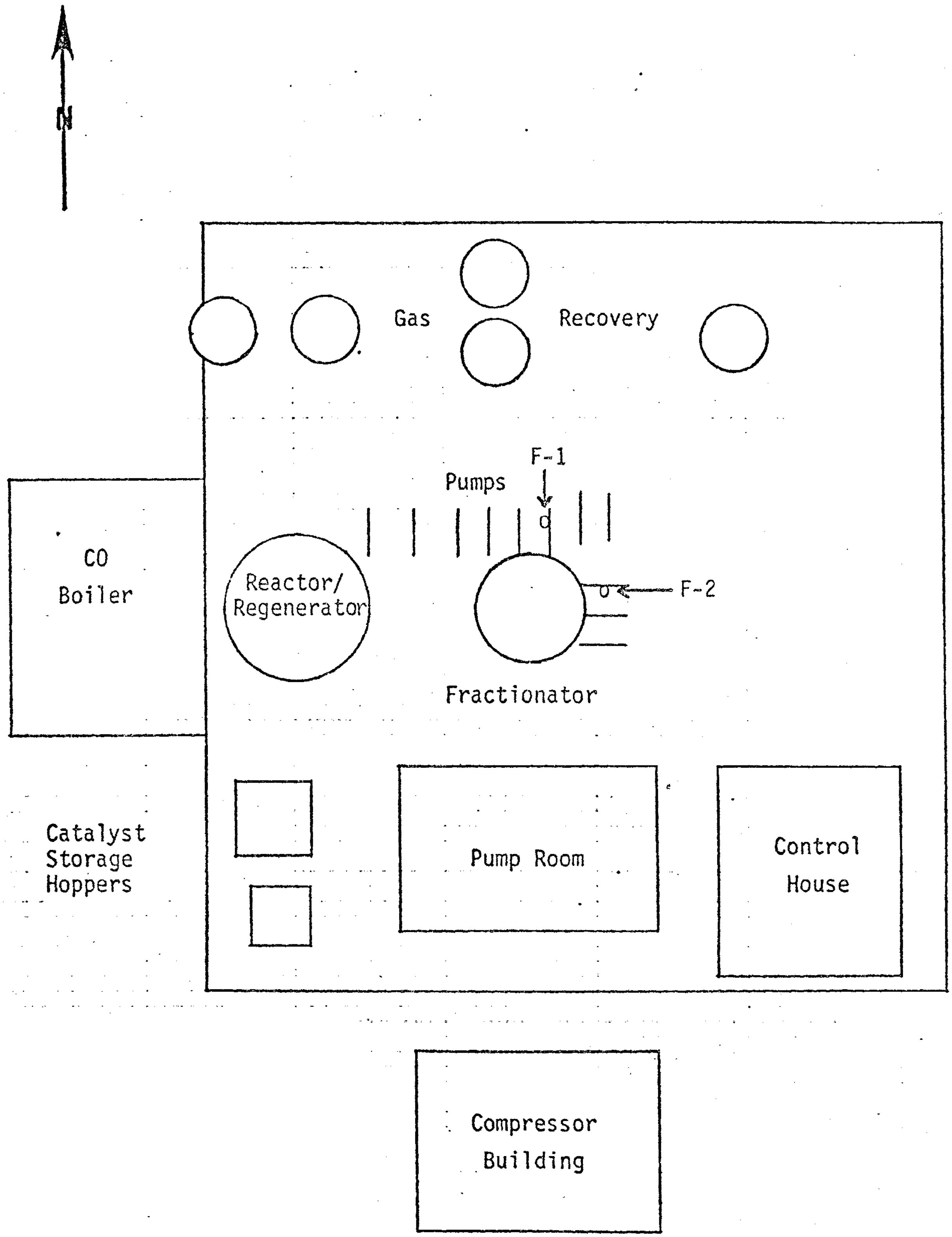

Figure IV-3. FCCU
Area Sampling Locations

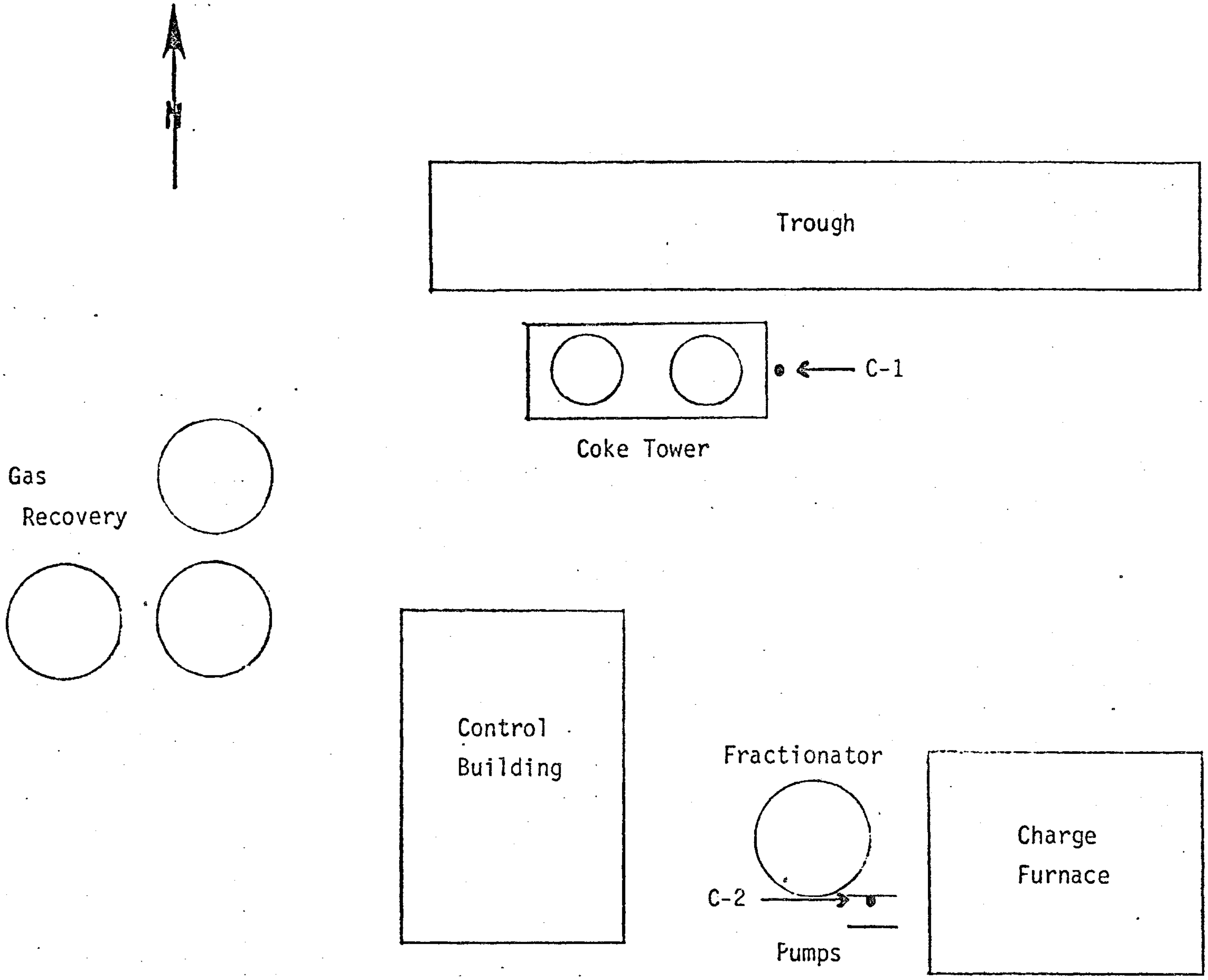

Figure IV-4. Delayed Coker Unit
Area Sampling Locations

B. Personal Sampling

The three operational shift workers and the four cutters were sampled during the day shift on November 30 and the evening shift on December 1. The cutting operation during the first day lasted from 0600 to 1000 and during the second day from 1800 to 2100.

ASPHALT PROCESSING UNIT

Location A-1, situated in the midst of several pumps near the vacuum tower, was sampled during the day shift on November 30. The sampling units were directly downwind of pump P-408, the vacuum bottoms pump which moved the charge to the asphalt blow still. Nearby was pump P-409, which moved dirty gas oil to storage tanks.

Location A-2 was sampled during the day shift on December 1. This was three yards downwind of the blowing tower and also downwind of pump P-18, which normally moved the blown asphalt to storage tanks.

V. RESULTS AND DISCUSSION

The complete results of the area and personal PAH samples collected at this Champlin refinery are presented in Tables V-1, V-2, and V-3. All 35 personal and area air samples analyzed from the three study process units had detectable quantities of at least five of the 23 PAHs or groups of PAHs for which the samples were tested. The cumulative PAH concentrations for individual samples ranged from less than 1 $\mu g/m^3$ for one area location in the delayed coker unit to as high as 150 $\mu g/m^3$ for a personal sample from one of the coke cutter helpers. The two upwind boundary samples were each less than 1 $\mu g/m^3$.

In general the cumulative PAH concentrations and number of PAHs identified were greater in the personal samples from the delayed coker unit than from the FCCU. The concentrations found in asphalt processing unit area samples were comparable to those found in the coker unit area samples, which were much higher than 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.

FCCU

The average (arithmetic mean) cumulative PAH concentration over the two shifts for the five FCCU workers was 22.2 $\mu g/m^3$ with the number of individual PAHs or groups of PAHs ranging from 10 to 18. Table V-4 shows that the operator and helper (outside operators) were exposed at the highest concentrations while the control room board operator was exposed at the lowest concentration (32.7 versus 13.3 $\mu g/m^3$).

TABLE V-1. PAH Analytical Results ($\mu g/m^3$) for Personal and Area Samples Collected at the FCCU**

	AREA (F-1)		AREA (F-2)		SHIFT FORMAN		BOARD OPERATOR		C.O. BOILER OP.		OPERATOR		HELPER	
	11/30	11/30	12/1	12/1	11/30	12/1	11/30 ††	12/1	11/30	12/1	11/30	†††	11/30	12/1
SAMPLE VOLUME SAMPLE TIME	Resp. 872 0625- 1435	Total 771 0745- 1456	Resp. 760 0719- 1431	Total 773 0719- 1431	912 0700- 1412	917 0653- 1416	941 0635- 1403	914 0656- 1422	990 0640- 1443	937 0650- 1414	906 0643- 1407		980 0631- 1441	939 0650- 1415
NAPHTHALENE*	2.04	5.03	5.11	1.91	4.59	3.41	1.95	4.35	3.82	4.58	8.85		10.29	8.23
QUINOLINE	0.42	1.08	0.34	0.18	1.26	0.48	0.65	1.04	1.49	--	2.52		1.35	0.64
2-METHYLNAPHTHALENE	6.76	13.23	8.28	6.64	5.66	6.45	2.65	8.22	8.40	8.63	11.45		10.43	10.89
1-METHYLNAPHTHALENE	3.50	6.87	5.09	3.35	3.18	3.27	1.47	4.51	4.34	5.13	7.08		7.55	7.38
ACENAPHTHALENE	--	0.09	0.02	0.11	--	0.01	--	0.03	0.07	--	--		0.28	0.20
ACENAPHTHENE	0.19	0.46	0.38	0.25	0.16	0.15	0.06	0.22	0.35	0.42	0.36		0.58	0.42
FLUORENE	0.24	0.46	0.47	0.27	0.18	0.13	0.07	0.22	0.35	--	0.40		0.51	0.34
PHENANTHRENE*/ ANTHRACENE*	1.84	3.09	4.08	1.87	0.81	0.42	0.29	0.54	1.29	1.00	1.52		2.34	1.48
ACRIDINE	--	0.58	0.42	0.35	0.03	0.04	--	0.08	0.23	0.06	0.09		0.13	0.13
CARBAZOLE	0.09	0.41	0.09	0.15	--	--	--	0.02	0.07	0.03	--		0.08	--
FLUORANTHENE	0.32	0.72	0.22	0.33	0.08	--	0.02	--	0.13	0.05	0.08		0.13	0.08
PYRENE*	1.33	1.80	1.60	1.62	3.17	0.03	0.10	0.04	0.48	0.14	0.34		0.67	0.33
BENZOFLUORENE	0.94	1.63	0.74	1.19	0.04	--	0.02	--	0.34	0.06	0.03		0.12	0.04
BENZ(a)ANTHRACENE*/ CHRYSENE*/TRIPHENYLENE	0.65	1.01	0.51	0.74	0.13	--	0.04	--	0.09	0.04	0.10		0.27	0.10
BENZO(e)PYRENE*/BENZO(a) PYRENE*	0.06	0.20	--	--	--	--	0.01	--	--	--	0.03		0.07	0.04
PERYLENE	--	0.09	--	--	0.01	--	--	--	--	--	--		<0.01	--
DIBENZ (a,j) ACRIDINE*	--	--	--	--	--	--	--	--	--	--	--		--	--
DIBENZ(a,i) CARBAZOLE*	--	--	--	--	0.04	--	<0.01	--	--	--	<0.01		<0.01	0.01
INDENO(1,2,3,-c,d)PYRENE*	--	--	--	--	0.01	--	--	--	--	--	--		--	--
DIBENZANTHRACENE * †	--	--	--	--	0.01	--	--	--	--	--	--		--	--
BENZO (g,h,i) PERYLENE	--	--	--	--	0.03	--	--	--	--	--	--		0.02	0.03
CORONENE	--	--	--	--	--	--	--	--	--	--	--		--	--
DIBENZPYRENE * †	--	--	--	--	--	--	--	--	--	--	--		--	--
TOTAL	18.38	36.75	27.35	18.97	19.42	14.39	7.33	19.29	21.45	20.14	32.86		34.82	30.35

* Suggested as having some cancer-causing potential.

** Blank values have been subtracted from data. Data have not been corrected for temperature and pressure variations; maximum deviation would be ± 2% of actual values. All personal PAH samples collected for total particulates.

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

†† Sampling was interrupted for undetermined period of time.

††† Employee refused to wear pump.

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

	AREA (C-1)		AREA (C-2)		DRILLER		Coke Cutters 1st HELPER		Coke Cutters 2nd HELPER		Coke Cutters CRANE OPER.		Operational OPERATOR		Operational 1st HELPER		Operational 2nd HELPER	
	11/30	11/30	12/1	12/1	11/30	12/1	11/30	12/1	11/30	12/1	11/30	12/1	11/30	12/1	11/30	12/1	11/30	12/1
	Total	Resp.	Total	Resp.														
Sample Vol.	833	819	748	744	533	314	527	246	499	272	576	403	957	918	943	845	944	871
Sample Time	0650-1438	0650-1438	1455-2153	1455-2153	0538-0958	1747-2018	0540-1002	1802-2005	0553-1000	1800-2012	0543-1020	1752-2105	0624-1402	1432-2147	0627-1405	1439-2143	0635-1411	1435-2138
NAPHTHALENE *	5.57	3.14	0.08	0.06	15.89	7.56	8.61	20.62	29.16	18.79	20.24	5.67	4.69	2.57	6.24	7.17	11.02	3.46
QUINOLINE	0.98	1.04	--	--	1.45	2.52	1.58	4.30	5.01	7.58	17.04	4.77	1.57	1.57	1.42	1.67	4.15	1.31
2-METHYLNAPHTHALENE	7.93	4.92	0.25	0.30	12.57	13.23	7.50	30.65	25.16	27.69	25.17	8.54	5.42	5.91	8.53	10.97	14.57	6.81
1-METHYLNAPHTHALENE	3.83	2.81	0.20	0.19	6.75	5.70	5.43	13.90	17.52	10.96	21.87	5.64	4.59	3.11	5.86	7.00	9.19	3.24
ACENAPHTHALENE	0.03	--	--	--	0.19	0.02	0.25	--	0.53	--	0.33	0.08	0.14	0.04	0.16	0.29	--	0.03
ACENAPHTHENE	0.14	--	--	--	0.26	0.37	0.34	0.55	0.78	--	0.72	0.17	0.36	0.20	0.26	0.47	0.43	0.17
FLUORENE	0.15	--	--	--	2.54	0.46	3.53	0.61	4.75	0.84	0.70	0.04	0.27	0.17	0.21	0.39	0.35	0.14
PHENANTHRENE/ * ANTHRACENE *	0.64	0.20	0.05	--	15.21	1.09	6.43	1.17	24.28	1.46	1.09	0.14	0.90	0.48	0.62	1.53	0.98	0.39
ACRIDINE	0.05	--	--	0.05	--	0.32	0.12	--	0.21	0.23	0.06	--	0.06	0.07	0.03	0.06	0.05	
CARBAZOLE	0.01	--	--	--	0.52	0.06	0.46	--	0.53	0.18	0.06	--	--	--	0.02	0.04	--	--
FLUORANTHENE	0.11	--	0.02	--	2.84	0.06	2.56	--	4.17	--	0.11	--	0.06	--	0.05	0.11	0.07	--
PYRENE *	0.80	0.23	0.13	0.04	10.84	0.30	5.86	0.33	14.58	0.31	0.33	--	0.21	0.09	0.16	0.33	0.22	0.04
BENZOFLUORENE	0.42	0.11	0.07	--	4.09	0.13	4.28	--	1.50	0.14	--	--	0.14	--	--	0.01	0.05	--
BENZ(a)ANTHRACENE/ * CHYRSENE/ * TRIPHENYLENE	1.38	1.00	0.07	--	5.03	0.13	7.41	0.15	9.96	0.27	0.13	--	0.04	--	0.02	0.04	0.04	--
BENZO(e)PYRENE/ * BENZO(a)PYRENE *	0.50	0.28	--	--	6.74	--	9.30	--	6.23	--	0.03	--	--	--	--	0.02	--	--
PERYLENE	0.27	--	--	--	--	--	0.91	--	0.59	--	--	--	--	--	--	<0.01	--	--
DIBENZ(a,j)ACRIDINE *	--	--	--	--	0.08	--	0.26	--	0.17	--	--	--	--	--	--	--	--	--
DIBENZ(a,i)CARBAZOLE *	--	--	--	--	0.05	--	0.16	--	0.17	--	0.01	--	<0.01	--	--	0.04	--	--
INDENO(1,2,3-cd)-PYRENE *	--	--	--	--	0.60	--	0.93	--	0.50	--	--	--	<0.01	--	0.03	0.01	--	--
DIBENZANTHRACENE *	--	--	--	--	0.78	--	1.53	--	0.80	--	--	--	--	--	--	--	--	--
BENZO(g,h,i)PERYLENE	0.11	--	--	--	2.12	--	3.43	--	1.99	--	--	--	0.01	--	<0.01	--	--	--
CORONENE	--	--	--	--	0.16	--	0.29	--	0.32	--	--	--	--	--	<0.10	--	--	--
DIBENZPYRENE *	--	--	--	--	0.77	--	1.27	--	1.02	--	--	--	--	--	--	--	--	--
TOTAL	22.92	13.73	0.87	0.64	89.47	31.95	72.44	72.28	149.94	68.46	87.93	25.05	18.45	14.22	23.62	30.15	41.12	15.58

* Suggested as having some cancer-causing potential.

** Blank values have been subtracted from data. Data have not been corrected for temperature and pressure variations; maximum deviation would be within ± 2% of actual values. All personal PAH samples collected for total particulates.

Table V-3. PAH Analytcial Results for Area Samples (μg/m³) Collected at Asphalt Unit and Upwind Locations**

	ASPHALT				UPWIND	
	AREA A-1		AREA A-2			
	11/30	11/30	12/1	12/1	11/30	12/1
	TOTAL	RESP.	TOTAL	RESP.		
SAMPLE VOL.	831	823	757	744	922	873
SAMPLE TIME	0703-1447	0703-1448	0734-1437	0734-1437	0724-1505	0656-1422
NAPHTHALENE *	2.14	1.27	0.33	0.59	0.40	0.29
QUINOLINE	1.49	0.55	0.13	--	--	0.07
2-METHYLNAPHTHALENE	8.04	4.71	1.12	1.59	0.19	0.04
1-METHYLNAPTHALENE	4.63	3.00	0.43	0.95	0.11	0.01
ACENAPHTHALENE	0.10	--	--	--	--	--
ACENAPHTHENE	4.55	0.52	--	--	--	--
FLUORENE	7.61	0.56	--	--	<0.01	--
PHENANTHRENE*/ANTHRACENE *	1.66	1.14	0.03	0.15	0.07	--
ACRIDINE	0.30	0.20	--	--	<0.01	--
CARBAZOLE	0.09	0.07	--	--	<0.01	--
FLUORANTHENE	0.03	0.05	--	--	0.02	--
PYRENE *	0.09	0.08	--	0.03	0.04	--
BENZOFLUORENE	--	--	--	--	--	--
BENZ(a)ANTHRACENE*/CHRYSENE*/TRIPHENYLENE	--	--	--	--	--	--
BENZO(e)PYRENE*/BENZO(a)PYRENE*	--	--	--	--	--	--
PERYLENE	--	--	--	--	--	--
DIBENZ(a,j)ACRIDINE*	--	--	--	--	--	--
DIBENZ(a,i)CARBAZOLE*	--	--	--	--	--	--
IDENO(1,2,3-cd)PYRENE*	--	--	--	--	--	--
DIBENZANTHRACENE*	--	--	--	--	--	--
BENZO(g,h,i)PERYLENE	--	--	--	--	--	--
CORONENE	--	--	--	--	<0.10	--
DIBENZPYRENE*	--	--	--	--	--	--
TOTAL	30.73	12.15	2.04	3.31	0.83	0.41

* Suggested as having some cancer-causing potential.

** Blank values have been subtracted from data. Data have not been corrected for temperature and pressure variations; maximum deviation would be within ± 2% of actual values. Upwind PAH samples collected for total particulates.

TABLE V-4. PERSONAL MONITORING RESULTS - FCCU

	No. of Samples	$\bar{X}$ (μg/m³)	PAHs
Outside Operators	3	32.7	14-18
Outside Operator - CO Boiler	2	20.4	11-14
Shift Foreman	2	16.9	10-17
Board Operator	2	13.3	11-13
Total	9	22.2	10-18

The results of the personal monitoring were quite consistent over the 2 days. There was less than 26 percent difference between the duplicate samples collected for the shift foreman, CO boiler operator, and helper. For the operator only a partial sample was collected for one shift. Both day shifts during which sampling was performed were termed as routine by the workers. The weather conditions were also fairly similar during both 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 36.8 μg/m³ (16 PAHs identified) and 19.0 μg/m³ (14 PAHs identified). For the duplicate sampling units with cyclones, the results were 18.4 μg/m³ (13 PAHs identified) and 27.4 μg/m³ (14 PAHs identified), respectively.

DELAYED COKER UNIT

Table V-5 gives a summary of the personal monitoring results for the seven coke workers. These values are again average cumulative PAH concentrations for the two sampling days. Table V-5 shows that the four coke cutters were exposed at higher concentrations than the three operational workers. However, the cutters normally do not work full 8-hour shifts; a normal cutting operation lasts up to 5 hours. The duration of the work shifts must also be considered when comparing relative exposure concentrations. Another difference noted was that the exposure levels were much higher on the first shift than on the second (69.0 vs 37.8 μg/m³). There were also more PAHs, particularly the heavier PAHs, identified during the first day's sampling. In fact, the two samples form the coke cutter helpers during the first day showed all 23 of the PAHs or groups of PAHs the analytical method was capable of detecting. The major difference identified between these two sampling days was that "needle" coke was cut the first day and "sponge" coke the second day. "Sponge" type coke is much softer and is produced more frequently than the "needle" type.

TABLE V-5. PERSONAL MONITORING RESULTS - COKER UNIT

	No. of Samples	$\overline{X}$ (μg/m³)	PAHs
Cutters*	8	74.7	8-23
Operational	6	23.9	9-18
Total	14	52.9	8-23

* Up to 5-hour work shift

The two area samples taken in the coker unit without cyclones showed cumulative PAH concentrations of 22.9 μg/m³ (17 PAHs identified) near the cutting operation and only 0.87 μg/m³ (8 PAHs identified) near the furnace charge pump. The duplicate area samples collected with cyclones showed cumulative concentrations of 13.7 μg/m³ (9 PAHs identified) and 0.64 μg/m³ (5 PAHs identified), respectively, for the same locations.

ASPHALT PROCESSING UNIT

The results of the area samples collected without cyclones (total mass) at the vacuum tower bottoms pumps was 30.6 μg/m³ (12 PAHs identified) and at the blowing still pump was 2.0 μg/m³ (5 PAHs identified). The duplicate area samples collected with cyclones were 12.2 μg/m³ (11 PAHs identified) and 2.9 μg/m³ (5 PAHs identified), respectively. As explained in the previous section, the actual blowing operation was not being performed during the survey.

PAH DISTRIBUTION

Table V-6 shows the percent distribution of PAHs found at the various units and upwind locations by compound ring number. As the table indicates, in all locations, at least 74.5 percent 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.

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

Ring No.	FCCU	Delayed Coker	Asphalt	Upwind
2	83.2	74.5	75.1	89.5
3	9.1	9.5	24.5	5.6
4	7.5	10.4	0.4	4.8
5	0.2	3.9	0	0
6	<0.1	1.6	0	0
7	0	0.1	0	0

In the coker unit some of the air samples showed higher proportions of the heavier molecular weight PAHs than in the majority of the samples. This was especially true for the personal samples for the driller and two helpers during the first cutting shift when "needle" coke was cut. Table V-7 shows the actual percentage distribution by ring number for these three samples.

TABLE V-7. DISTRIBUTION (%) OF PAHs FOUND BY RING NUMBER

Ring No.	Coke Driller and Helpers (first shift sampled)
2	44.6
3	21.9
4	20.4
5	8.9
6	4.1
7	0.2

VI. CONCLUSIONS

The results of the personal, area, and upwind air samples from the Champlin refinery 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 processing areas during restricted operations; however, the results of these area samples indicated that worker exposure to detectable quantities of of PAHs probably also exists in these areas. In attempting to draw conclusions from this survey, one must keep in mind that the samples were only 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 (except as noted in asphalt processing) that would cause one to believe that these results were not representative of these units.

There was a trend in the personal sampling results 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 to a variety of different PAHs greater than anticipated. The four coke cutters appear to be the work group exposed at the highest PAH concentrations during their work shift, even though their shift lasts only three to four hours at a time. The results for the other workers at the coke unit (the three operational workers) were comparable to those for the FCCU workers. At the FCCU, the personal sampling data were quite similar over the two sampling shifts; while at the coke unit, in general the concentrations were higher during the first shift, especially for the coke cutter group. The primary difference noted between the two shifts was that "needle" type coke was cut the first day and "sponge" type the second.

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 the personal samples in general 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 indicate that the heavy fraction pump area is a source of PAH emissions. In the coke unit the downwind sample from the cutting operation also indicated, as expected, that the cutting operation generated airborne PAHs. The other sample area location in the coke unit (fractionator bottoms pump) only yielded concentrations comparable to the upwind samples, indicating that it was not a major PAH source.

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 collected during the cutting of "needle" coke had all 23 PAHs identified. As expected from Phase II results, the great proportion of the PAHs identified were the lighter 2- and 3-ring compounds. However, considerable quantities of 4-, 5-, and 6-ring PAHs were found in the coke cutter personal samples mentioned above.

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 makes 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. In the coker unit, both area locations sampled yielded higher PAH concentrations in the total mass sample, as expected. However, in both the FCCU and asphalt unit, one 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

Opening Conference Attendees

Enviro Control, Inc.

Stan Futagaki	Senior Industrial Hygienist
Edward Haggerty	Industrial Hygienist

NIOSH

Clinton Cox	Project Officer

Champlin Petroleum Company

Paul D. Fritz	Refinery Superintendent
Joe F. Gay	Corporate Director of Safety and Loss Control
Chester Shockley	Safety Manager
Tim Sodowsky	Safety Engineer
E. J. Dougherty	Manager of Operations
Jim Bolliger	Manager of Technical Services
Orie Dean Robison	Manager of Maintenance