PHASE III SURVEY REPORT #7

WORKER EXPOSURE TO POLYAROMATIC HYDROCARBONS AT SELECTED PETROLEUM REFINERY PROCESS UNITS

SURVEY LOCATION:

STANDARD OIL COMPANY OF OHIO
TOLEDO, OHIO

Survey Dates:

28-30 MAY 1980

Report Date:

OCTOBER 1980

DISCLAIMER

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

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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 blower unit. The group of operators who have responsibility for all of the north-side units which include the FCCU and delayed coker unit were also sampled. A silver-membrane filter followed by Chromosorb 102 was used for sampling, and analysis for 23 individual or groups of PAHs was performed by gas chromatography/mass spectrometry. All 25 of the personal and area air samples had detectable quantities of at least seven PAHs or groups of PAHs, with the cumulative PAH concentration for individual samples ranging from 1.6 $\mu g/m^3$ for a personal sample from one of the north-side operators to as high as 57.4 $\mu g/m^3$ for one location in the FCCU. The two upwind boundary samples were 1.11 and 0.05 $\mu g/m^3$.

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I. INTRODUCTION

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

- Phase I: A detailed literature search was performed including the industrial hygiene aspects and the potential occupational health problems associated with this industry. Preliminary fact-finding surveys were conducted at three refineries. This phase culminated in a preliminary study protocol which recommended the investigation of potential carcinogens in three types of refinery process units: the fluid catalytic cracker, 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 three study process units.

- Phase III: The objective of this main phase of the study is to characterize worker inhalation exposure to PAHs in the 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 the previous three phases.

Phase III is currently in progress. The Standard Oil Company of Ohio (SOHIO) refinery at Toledo, Ohio, was the seventh refinery visited as part of Phase III, and this report presents the information and air-sampling data for PAHs collected during that survey.

The Phase III industrial hygiene survey of the SOHIO refinery was conducted over a period of 3 days, May 28-30, 1980. The morning of the first day was devoted to opening conferences and a walk-through of the study process units; the personal and area air-sampling program was carried out during all 3 days. All arrangements for this visit were made through the corporate industrial hygienist.

The opening conferences were held with representatives from the refinery (including a representative of the Oil, Chemical, and Atomic Workers International Union), the refinery corporate office, 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 3 days. After the meetings, the survey team conducted a walk-through of the fluid catalytic cracker unit (FCCU) and the asphalt blowing unit, two of the three units to be sampled. At the FCCU, where personal monitoring was scheduled, the Enviro industrial hygienists explained the sampling procedures to the unit supervisors. Because of the coke-cutting schedule during the 3 days of the survey, it was necessary to omit the walk-through of the delayed coker unit and instead to sample the delayed coker during the evening shift (1500-2300) of the first day.

The complete sampling schedule included area and personal sampling at the delayed coker unit the first day and also during the day shift of the third day. At the FCCU, area and personal samples were collected during the day shifts of the second and third days as scheduled. At the asphalt blowing unit, only area samples were collected during the day shift of the third day.

II. DESCRIPTION OF REFINERY

This SOHIO refinery is located on the east side of Toledo, Ohio, near where the Maumee River flows into Lake Erie. With its crude capacity of 120,000 bbl/day, it is classified as a "large" refinery for the purposes of the study. Since the oil company that owns this refinery and one other is one of the largest 15 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 was originally built in 1911 by Standard Oil; almost all of the major process units have been rebuilt since 1958. Currently the refinery occupies about 450 acres and produces a full line of petroleum products which includes:

- propane
- butane
- hydrogen
- gasoline
- fuel oils (No. 2)
- Diesel oil
- kerosene
- sponge and needle coke
- asphalt

Most of the crude refined here is a mixture of foreign crudes. During the survey the crude being refined at the No. 1 unit was a combination of North Sea, Zuetina, Trinidad, East Texas, Michigan, and several others categorized together as a "sweet" (0.3-0.4% sulfur by weight), "mixed base" (containing both paraffins and naphthenes) crude with an API Gravity Index of 40.3. The crude refined at the No. 2 unit was primarily Arabian with small percentages from Texas and Trinidad. This crude was categorized as a "sour" (1.3-1.5% sulfur by weight), "mixed base" crude with an API Gravity Index of 34. Most of the crude is received by pipelines; most of the products are shipped by pipeline, barges, and railcars.

The major process units at the SOHIO refinery include:

- two crude distillation units
- two vacuum distillation units
- two catalytic reformers
- three alkylation units
- two isocracking units
- FCCU
- asphalt blower unit
- catalytic polymerization unit
- delayed coker unit
- hydrogen production unit
- naphtha treater
- sulfur recovery

There is one main control building ("nerve center") located west of the FCCU and naphtha treater, and several smaller control buildings ("satellites") located throughout the production areas. Figure II-1 shows a rough refinery plot plan of the major units.

There are approximately 380 hourly employees that belong to the union (OCAW) and an additional 180 that are salaried (supervisory 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.

The safety and health staff at this refinery includes the safety director, fire protection specialist, health and safety specialist, general safety specialist, security and safety officer, and the plant nurse. The nurse is on the premises from 0730 to 1600, 5 days a week. All newly hired employees undergo an 8-hour Red Cross first aid training session; in addition, a small number of employees (especially safety personnel) have been trained in cardiopulmonary resuscitation. The dispensary and treatment room is fully equipped to handle first aid situations and various routine

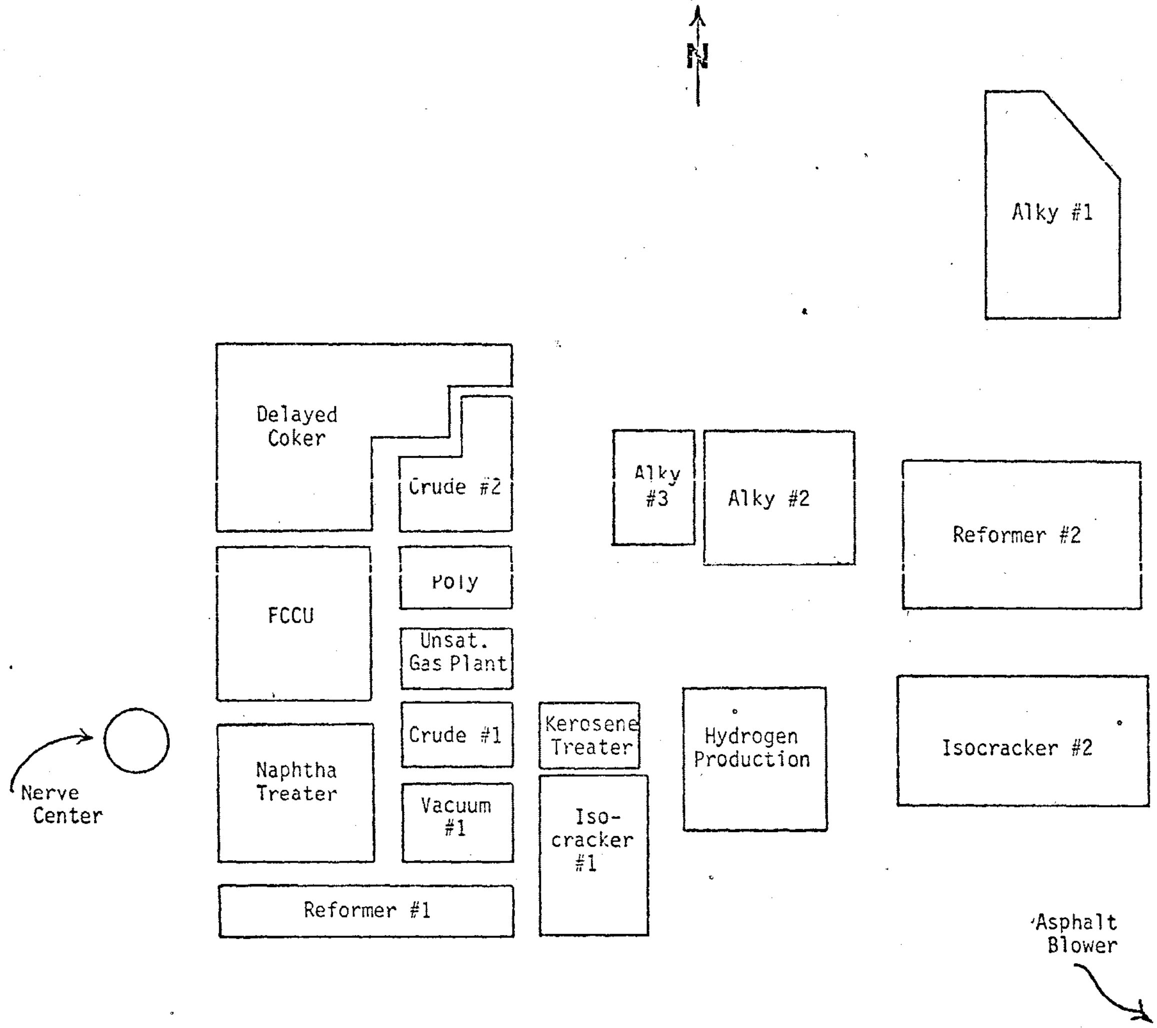

FIGURE II-1. Refinery Main Production Area examinations. All of the production workers are given preplacement medical examinations; periodic examinations are given at least once every 5 years. Physical examinations are given by a physician hired by the company.

As part of good industrial hygiene practice, the use of protective clothing and equipment (e.g., hard hats, safety shoes, long-sleeved shirts, eye protection) is emphasized. Eating is allowed in most control rooms; smoking is not allowed in the production or storage areas. All new employees attend an extensive training session over a 1-week period which includes information on unit equipment, operations, respirator use, safety hazards, fire protection, and first aid. New employees usually spend their first year in maintenance where formal training continues, and then, once on a unit, the new operators are trained for at least another 2 months on the job. Good unit housekeeping is practiced as an important means of minimizing worker exposure to potential hazards. Spills are promptly cleaned up by the unit operators, and any necessary equipment or structure repair is promptly carried out by the unit operators or in-house maintenance crews.

The safety staff is responsible for the industrial hygiene sampling. Although a routine sampling schedule is not yet established here, a considerable amount of monitoring is conducted upon request, for compliance purposes, and for any other reasons felt necessary by the refinery personnel.

III. STUDY PROCESS UNITS

FLUID CATALYTIC CRACKER UNIT (FCCU)

A. Unit and Process Description

The FCCU is located on the west side of the main refinery production area (Figure II-1), south of the delayed coker unit and north of the naphtha treater. The present unit, including the CO boiler, was built in 1958 and currently has a production capacity of about 55,000 bbl/day.

The unit is divided into two main sections, FCC #1 and FCC #2, that together occupy an area about 250 x 200 feet (Figure III-1). FCC #1 includes the CO boiler, side-by-side reactor/regenerator (R/R) structure, fractionator, two catalyst hoppers, and numerous pumps (including several heavy-fraction pumps). FCC #2 is located to the north of FCC #1 and includes the air blower, gas compressors, numerous heat exchangers, pumps, and drums. Most of the process streams in FCC #2 are the lighter fractions. The unsaturated gas plant is located east of FCC #1 and includes gas recovery structures such as the secondary absorber, gasoline splitter, depropanizer, gasoline and other distillate treaters, and numerous pumps. The unsaturated gas plant is considered a separate unit from the FCCU and is run out of a different control room by separate operators.

There is a long, enclosed building to the west of FCC #1; this building houses numerous compressors and a separate work station for the two FCCU operators. South of this long building is the main control building ("nerve center") for the FCCU, delayed coker, and several other units located in this area.

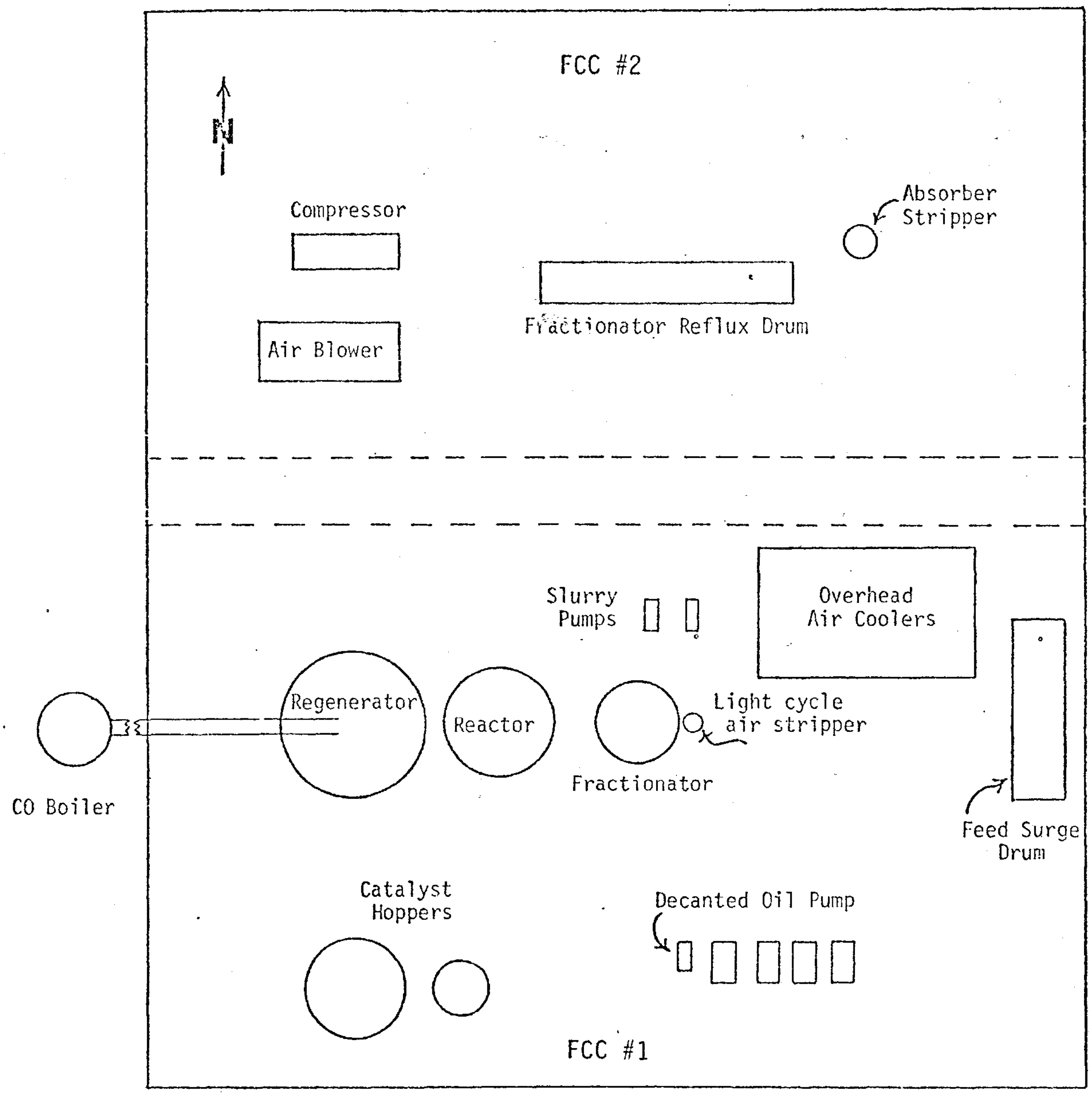

FIGURE III-1. FCCU

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

This fresh feed plus slurry recycle 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 1,200°F (649°C). 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 main products from the fractionator are:

- butane
- isobutane (alky feed)
- propane
- propylene
- cat gasoline
- light cat gas oil (furnace oil)
- decant oil

B. Work Force

There are normally only two operators (one each for FCC #1 and FCC #2) assigned full time to the FCCUs during each shift. Both operators work out of the small work station in the long building just north of the nerve center. In addition, there are three workers who have responsibilities for all "north-side units," including the FCCU. These three north-side workers operate out of the nerve center. Following is a brief description of the activities of these five workers.

- FCC #1 Operator: Performs the routine outside tasks for the FCC #1 section. This includes maintaining the numerous pumps, taking temperature and pressure readings, supplying and adding fresh catalyst, and periodically patrolling the entire FCC #1 section to detect any leaks or malfunctions. Performs minor cleanup and maintenance tasks. He also collects spent catalyst and process stream samples (e.g., decant oil, slurry recycle, fresh feed, light gas oil, heavy gas oil). Spends about 60% of the shift in the FCC #1 area and the rest in the work station.

- FCC #2 Operator: Performs outside duties similar to those of FCC #1 operator for FCC #2 section. Duties include regulating valves, pumps, compressors, and auxiliary equipment to direct flow of products; checking temperature and pressure gauges and flow meters; and patrolling the section for any malfunction. Spends about 60% of the shift in the FCC #1 area and the rest in the work station.

- North Inside General Operator: Spends essentially 100% of his shift inside the nerve center, monitoring and logging in the various meters and charts on the control board.

- North Outside General Operator: Lends assistance to the operators on any of the north-side units; this includes the FCC #1, FCC #2, unsaturated gas plant, polymerization, cokers 1 and 2, crude vacuum No. 2, and the cooling towers. This requires a very experienced operator who knows how to perform all of the various tasks on the north side. Normally spends about 90% of his shift outside.

- North Operating Foreman: Monitors and supervises the operations of the north-side process units. Periodically visits each unit, checking with the various unit operators for any problems or unusual conditions. His responsibility is to ensure the smooth operations of these units. Can answer technical questions, direct emergency procedures, or provide communications to any of the other refinery sectors. This foreman spends about 95% of his shift outside.

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 during sampling of the various streams, during maintenance and housekeeping activities, from fugitive emissions, and from the regenerator flue gas.

Sample bombs and the open-spigot-and-bottle method are used to collect process samples at this unit. Sample bombs are used to collect the light-fraction gases (e.g., propane, butane, isobutane); these samples are collected by laboratory technicians and are taken to the laboratory for analysis. The liquid process streams samples, including several heavy-fraction streams (e.g., decant oil, slurry recycle), are collected by the unit operators by the open-spigot-and-bottle method. Sampling loops are not used; the sample lines are flushed directly into the sewer system. The only type of control measure used for this type of sampling is the water cooling of hot liquid samples before collection. This reduces sample vaporization during sampling. Although the operators normally perform the sampling quickly and without skin contact, this is a definite potential source of PAH exposure.

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 crews (e.g., pipefitters, electricians) that provide preventive and repair services. The last major turnaround for this unit was in 1977.

Hard hats, safety shoes, eye protection, and long-sleeved shirts are required on this unit. 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, NIOSH-approved air-purifying and self-contained breathing-air respirators are available. These respirators are maintained by the refinery safety department and the unit operators.

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 close together near the fractionator tower. This is an area where PAH concentrations might be elevated. The operators' work station and the nerve center are both air-conditioned but not under positive pressure and are occasionally downwind of the R/R, fractionator, and heavy-fraction pumps.

The flue gas from the regenerator goes through a series of cyclones to remove catalyst fines and is then burned in the CO boiler with an auxiliary fuel. The CO boiler removes not only 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 at the north end of the refinery production area. The FCCU is to the south and the No. 2 crude and vacuum units are to the south and east. There are actually two separate delayed coking units within the one area. Coker #1, built in 1958, has two 89-foot coke drums with a daily production capacity of about

440 tons of sponge coke. Coker #2, built in 1966, has two 64-foot coke drums with a daily capacity of 240 tons of needle coke.

The unit is spread over an area of about 500 x 250 feet with the No. 2 crude vacuum unit in the southeast corner of the unit (Figure III-2). Both coke towers (open, multilevel structures that include the coke drums) are at the north end of the unit; parallel railroad tracks run beneath each pair of drums. Both sets (coker #1 and coker #2) of charge furnaces, charge furnace pumps, and fractionators (bubble towers) are to the south of the coke towers and railroad tracks. The single control building, also housing the locker and tool room, is located about 30 feet south of the coker #2 charge furnace. The blowdown drum and containment pit are located about 200 feet east of the coke towers.

Coker #1 produces a #2 grade coke referred to as sponge coke. The residual from the vacuum units is pumped from storage to the coker #1 fractionator where the lighter fractions are separated and recovered. The bottoms from the fractionator are then pumped (furnace charge pump) to the gas-fired furnace where they are heated to about 900°F (482°C). The heated charge then goes to one of the two coker #1 drums where the thermal cracking process begins. Each drum has a 48-hour cycle with coke formation lasting about 24 hours. One coker #1 drum is cut about every 24 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 coker #1, other than sponge coke, include: fuel gas, gasoline, intermediate distillate, and FCCU charge (gas oil).

Coker #2 produces a #1 grade coke referred to as needle coke, a higher quality coke that is much harder and denser than the sponge type. The unit utilizes a difference feedstock from coker #1, and the operating parameters, temperature and pressure, are also different. Otherwise the two units are quite similar in operation with each drum operating on a 48-hour cycle. The products from coker #2, other than needle coke, include: fuel gas, propane/butane fraction to crude overhead receiver, and FCCU feed (gas oil).

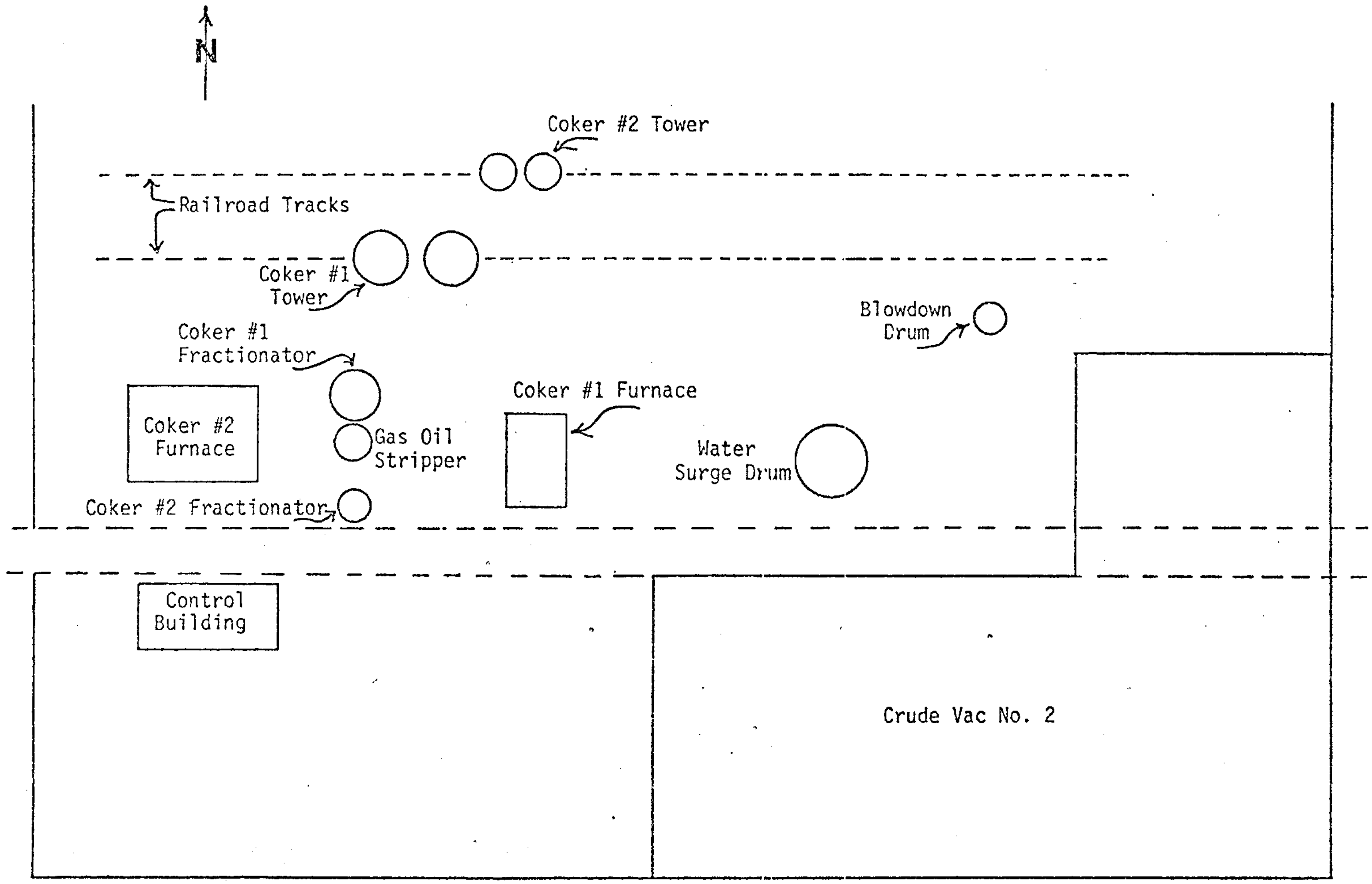

FIGURE III-2. Delayed Coker Unit

A complete cycle of each drum from heating to cutting is 48 hours. About 9 hours before the cutting operation is scheduled, coke formation (24 hours) is stopped by switching the feed to the other drum. In 1 hour, steam is introduced into the drum to cool it. This lasts about 2 hours, and then water is added to further cool the drum (6 hours). Nine hours after the feed is switched, the top and bottom of the drum are opened; and the coke is cut with a high-pressure hydraulic bit. An initial hole is bored through the coke (1-1½ hours) and then the coke is cut from the bottom up (3-4 hours). Railroad cars are positioned directly beneath the drums to provide direct loading as the coke is cut.

After cutting is completed, the top and bottom of the drum are replaced: the drum is pressure-tested for seal, heated, and is ready to begin coke formation when the feed is switched from the other drum. The entire cutting operation normally lasts up to 8 hours.

B. Work Force

The work force for the delayed coker unit is divided into two groups, the operational group and the coke-handling group. The two-person operational group works the normal 8-hour shift; following is a brief description of their job activities.

- Coker #1 Operator: This operator and the coker #2 operator perform all of the routine outside tasks for this unit. The coker #1 operator has responsibility for the areas including the coke tower, furnaces, containment pit, and jet pump area. Performs visual inspection tours of this area four times per shift, checking for leaks, spills, or any malfunctions that may create an unsafe condition. These tours usually last from 15 to 30 minutes. Other duties include meter and gauge readings, valve switching, and also monitoring and logging in the various charts and gauges in the control room. Normally spends about 50% of the shift outside in the production areas.

- Coker #2 Operator: Has responsibility for the various pumps, fractionators, and other gas recovery towers and equipment. Duties include visual inspection of equipment, meter and gauge readings, starting and shutting down pumps, lubricating and oiling pumps, and sample collecting. Eight process streams are normally sampled each day shift; these streams include light distillate, intermediate distillate, gas oil, furnace charge, and decant oil feed. This operator normally spends about 50% of the shift outside in the production areas.

The coke-handling group is normally made up of the driller and three others during the day shift; during the evening shift (1500-2300), there is one less worker. Following is a brief description of their job activities.

- Driller: Deheads the top of the drum with or without help and sometimes helps with the bottom. The great majority of the shift is spent at the drilling station in the coke tower penthouse. It takes about an hour to make the initial "bore-through" and then the bit is switched for the actual cutting, which lasts about 2½ hours for sponge coke and 5-6 hours for needle coke. He then helps to close the drum and with the general cleanup operations.

- #2 Cleaner: Acts as the relief man and assistant to the driller and #3 cleaner. Periodically takes over the drilling operation in the penthouse, allowing the driller to take breaks. Most of his shift is spent down below on the second level (deheading the drum bottom, directing the loading of the railcars) or on the ground level cleaning up the general area of loose coke.

- #3 Cleaner: Helps with the opening and closing of the drum bottom and positioning of the movable platform at the start of every cutting operation. During much of the cutting operation, he is positioned in an enclosed shelter, level with the top of the railcar. From here through a window, he regulates the movement of the cars (by motorized winch) to allow even loading of the cars. Cleanup is ongoing during cutting, but everyone helps once the cutting is completed. Large pieces on the ground are either picked up or shoveled, and the whole area is hosed down.

- #4 Cleaner: Primary duties are to help and relieve the #3 cleaner; this can include deheading the bottom, directing the railcar loading, and cleaning up the ground level. He also greases and oils the winch and motor and other equipment.

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 coke handlers must clean and prepare the fittings, and at this particular unit, ensure that the railcars are properly loaded, and clean up 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 and handling equipment such as front-end loaders and trucks. However, this method requires that at least one of the coke handlers be stationed at the drum bottom area to ensure proper railcar loading. Although in an enclosed station, this worker 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 driller normally opens and closes the top of the drum by himself; this takes about 30 minutes. At least two of the coke handlers work as a team to position the hydraulic supports, drop the bottom of the drum, and move the sliding platform to the side. This normally takes about 45 minutes. No metal sleeve or chute extender is used at this unit; the coke falls directly from the drum into the railcar.

The two penthouses on the top level are relatively enclosed one-room buildings (45 x 20 feet) where the driller operates the overhead drills. There are two openings in the roof and several windows; however, natural ventilation did not appear to be good. It can also get very hot in these rooms. The drillers attempt to keep the top of the drum as covered as possible to minimize any vapor or particulate escape into the penthouse during the drilling operation. This is done by positioning wooden panels around the drill shaft.

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 is done during cutting,and also after it is finished.

All workers on this unit wore hard hats, safety shoes, and at least long-sleeved shirts. Some of the coke handlers wore coveralls that are provided by the company. These coke handlers changed into their coveralls or separate work clothes in their small locker room in the same building and adjacent to the unit control room. Shower facilities are located at the front of the refinery. There were no routine operations that required the use of respirators; however, 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 room. Neither room was under positive pressure; the control room was air-conditioned. Because of the changing wind direction at this refinery, the control building is occasionally downwind of the coke tower and production area.

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

ASPHALT BLOWING UNIT

A. Unit and Process Description

The asphalt blowing unit is by itself about ½-mile from the main production area in the southeast corner of the refinery. This unit is not shown in Figure II-1. There are two blowing towers side-by-side with a production capacity of 7,000 barrels of blown (oxidized) asphalt per day.

The unit (Figure III-3) is a relatively small (250 feet x 120 feet), simple unit with the main structures being the control building, the air blower (compressor), the two blowing towers, the asphalt vent gas knockout drum, and the asphalt fume incinerator. There are also several pumps including the two asphalt product pumps. The unit foundation is gravel.

The feed to the blowing towers comes from storage tanks (vacuum bottoms) and enters the two vertical vessels at several points in the upper half. The compressed air is discharged into the bottom of the towers and oxidizes the asphalt. The vent gas first goes to a knockout drum to remove any entrained mist and particulates and then to the fuel-oil-fired incinerator. The asphalt product is pumped to storage.

B. Work Force

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

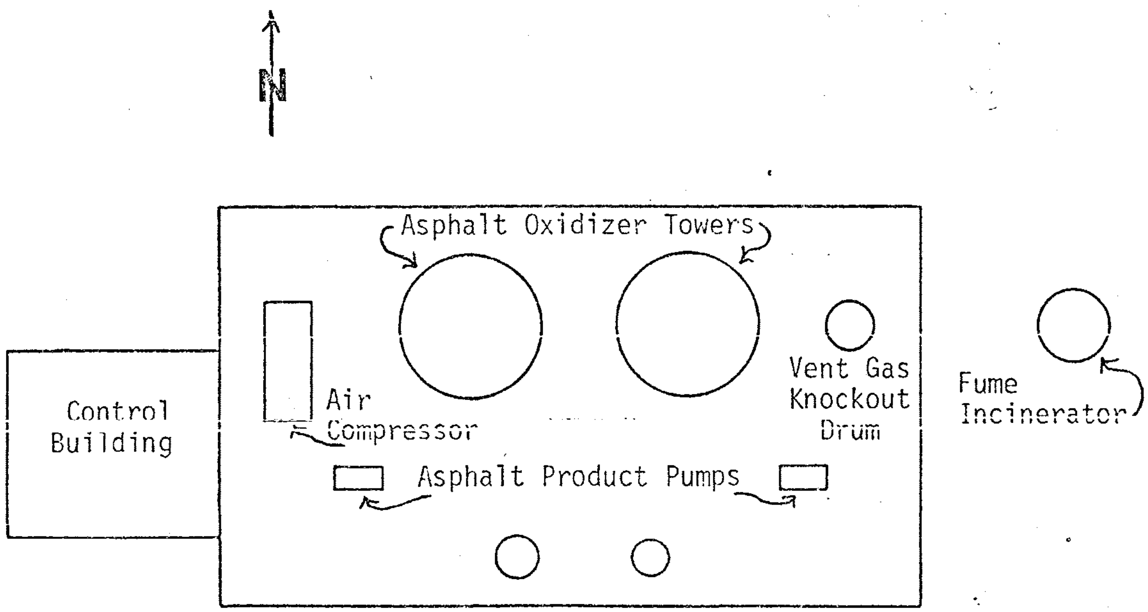

FIGURE III-3. Asphalt Blowing Unit

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 SOHIO refinery. Although all sampling was scheduled for the day shifts of the second and third days, an adjustment to the original sampling plan was made to allow sampling during the cutting of both types of coke (sponge and needle) produced here. The first shift sampled at the delayed coker unit was the evening shift (1500-2300) of the first day (May 28). Needle coke was cut from the east drum of coke tower #2. The day shift of May 30 was the second shift sampled at the delayed coker; sponge coke was cut from the east drum of coke tower #1 during this shift. The sampling schedule at the FCCU did not change.

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 Model S pump calibrated at approximately 2.0 ℓ/minute. To investigate the size distribution of airborne particles in the study process units, a total particulate area air sample was collected at each sampling site for optical sizing. These samples were collected using an open-face cassette containing a mixed cellulose ester filter (0.45-μm pore size) and a portable MSA Model S pump calibrated at 2.0 ℓ/minute. A modified sampling device (Figure IV-2) was used for personal monitoring for PAHs. The Chromosorb 102 was packed in a glass tube following the cassette rather than in the cassette itself. An upwind sample was collected each sampling day on the south boundary line (Cedar Point Road). A total of 25 samples were 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

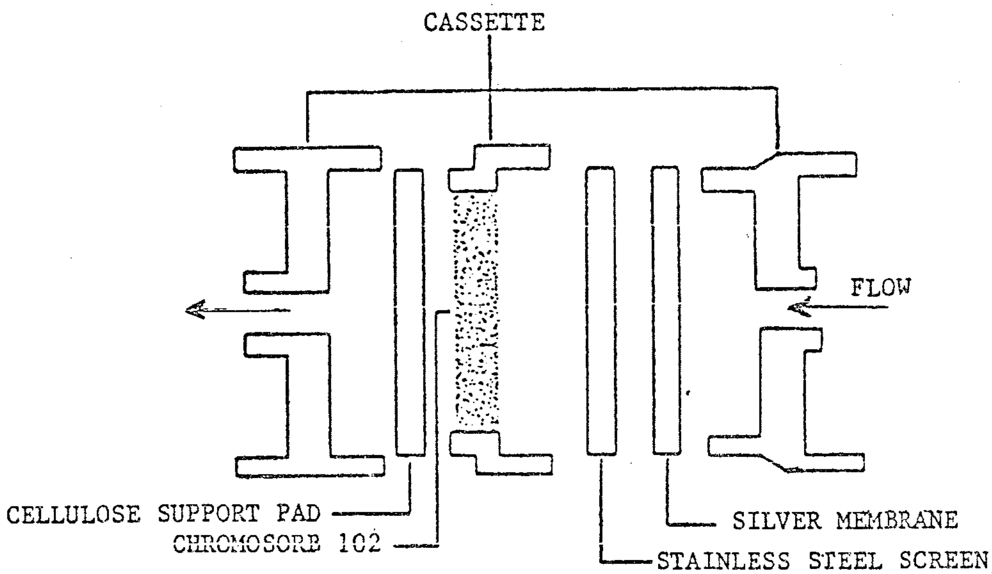

FIGURE IV-1. Area Monitoring Device for PAHs

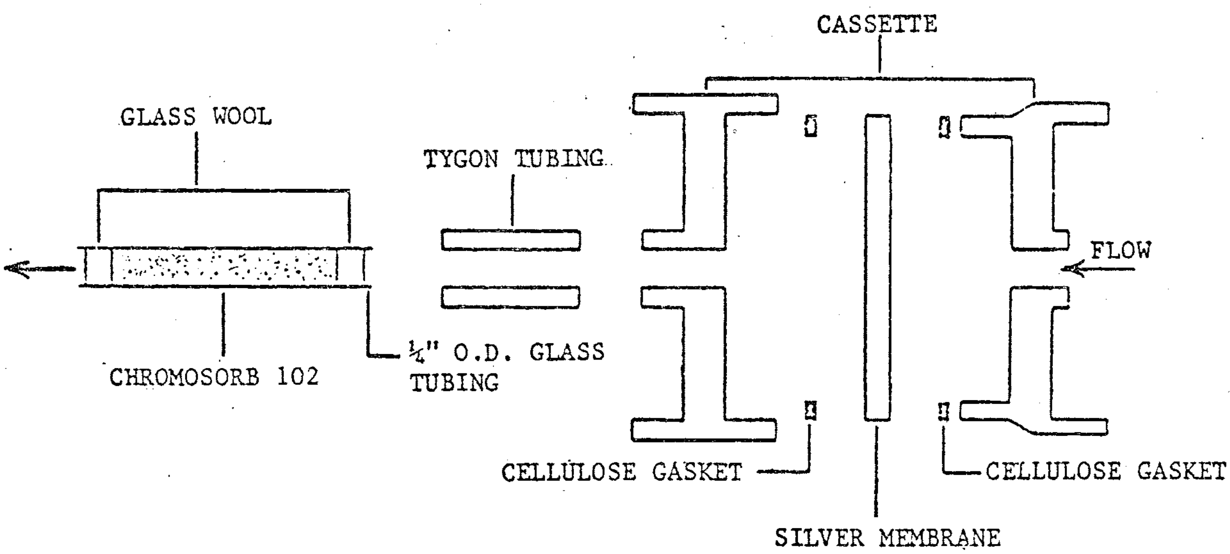

FIGURE IV-2. Personal Monitoring Device for PAHs resolve some of the groups of PAHs. This difference reduced the number of individual, or groups of, PAHS for which the method is capable of analyzing, from 27 to the 23 listed below.

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

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

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

SAMPLING CONDITIONS

Weather conditions for the first sampling shift at the delayed coker unit (evening shift on May 28) were clear skies with the temperature ranging from 88°F (31°C) at 1600 to 78°F (26°C) at 2200. The relative humidity during this period ranged from 26 to 42% and the winds were steady out of the southwest at 5-10 mph.

Weather conditions for the day shift on May 29 were light rain in the early morning clearing by 0800. The temperature ranged from 65°F (18°C) at 0730 to 85°F (29°C) at 1330, while the humidity ranged from 70% down to 45% during this period. During the morning, the winds were out of the southwest at 5-7 mph; at about 1300, the wind direction became erratic.

On May 30, the sampling shift started with partly cloudy skies becoming dark and overcast by 0800; by 0840, the skies started to clear and remained partly cloudy for the remainder of the shift. The temperature ranged from 68°F (20°C) at 0630 to 84°F (29°C) at 1330. The relative humidity ranged from 73% down to 59%, and the winds were out of the southwest at 3-8 mph, gusting to 12 mph.

FCCU

A. Area Sampling

Two locations near heavy-fraction pumps (Figure IV-3) were selected for collection of area samples in the FCCU. Location F-1 was about 3 feet above the slurry recycle pump and 15 feet north of the fractionator. This centrifugal pump moves the bottoms from the fractionator, which include spent catalyst, back to the reactor. Location F-2 was about 3 feet above the decanted oil pump which is located about 40 feet south of the fractionator. Location F-1 was sampled during the day shift on May 29 and F-2 during the day shift on May 30.

B. Personal Sampling

Both FCCU operators, FCC #1 and FCC #2, were sampled during the day shifts on May 29 and 30. In addition, the north inside general operator, the north outside general operator, and the north outside foreman (described in Chapter III) were also sampled during these two shifts.

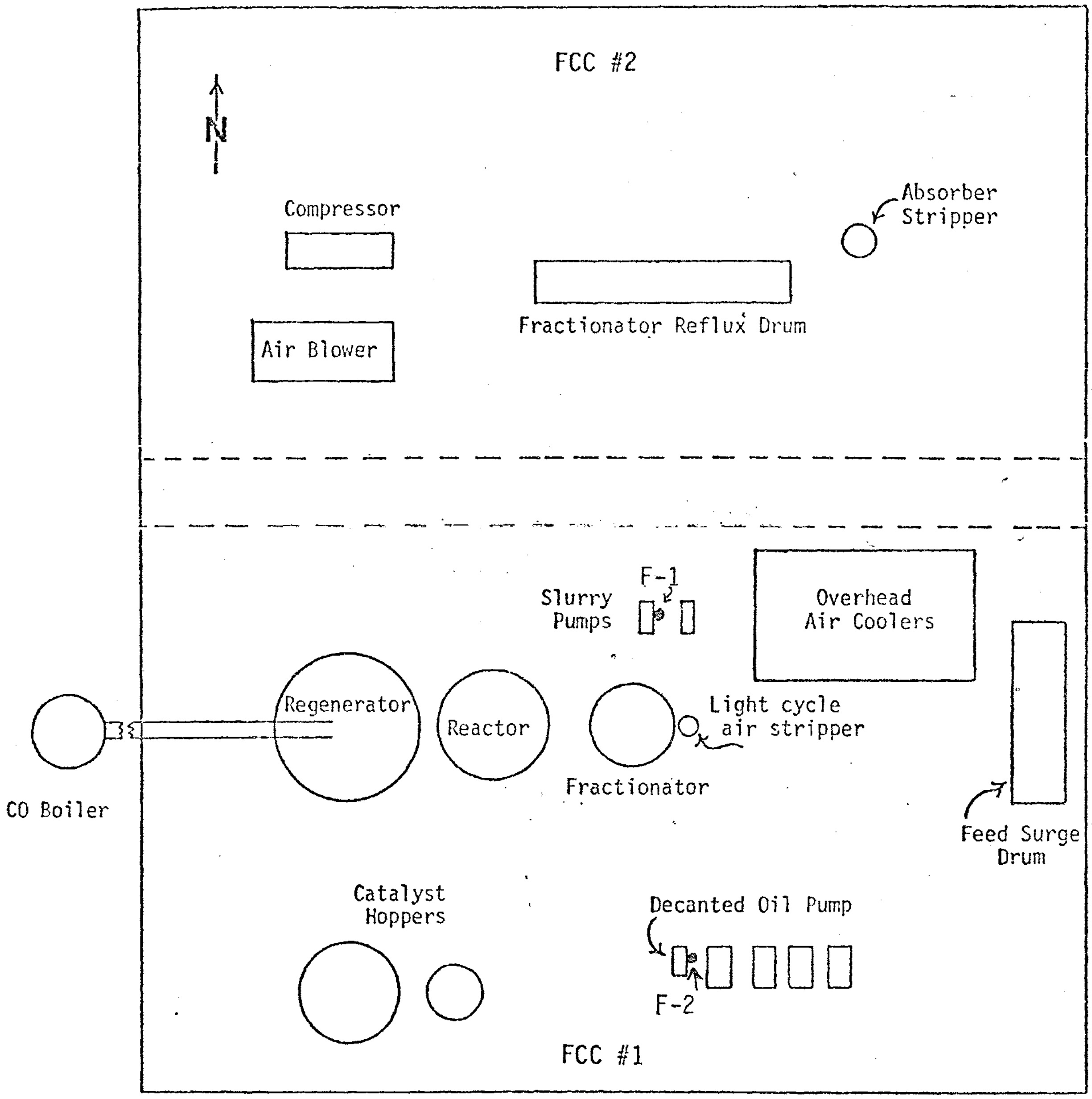

FIGURE IV-3. FCCU Area Sampling Locations

DELAYED COKER UNIT

A. Area Sampling

Figure IV-4 shows the two area sampling sites selected at the delayed coker unit. Location D-1, about 20 yards northeast and downwind of the drum being cut (east drum of coke tower #2), was sampled from 1500 to 2300 on May 28. The sampling units were positioned on a walkway about 6 feet above ground level. Location D-2 was about 20 yards northeast and downwind from the drum being cut (east drum of coke tower #1) on May 30 during the day shift. The sampling units were positioned about 5 feet above ground level.

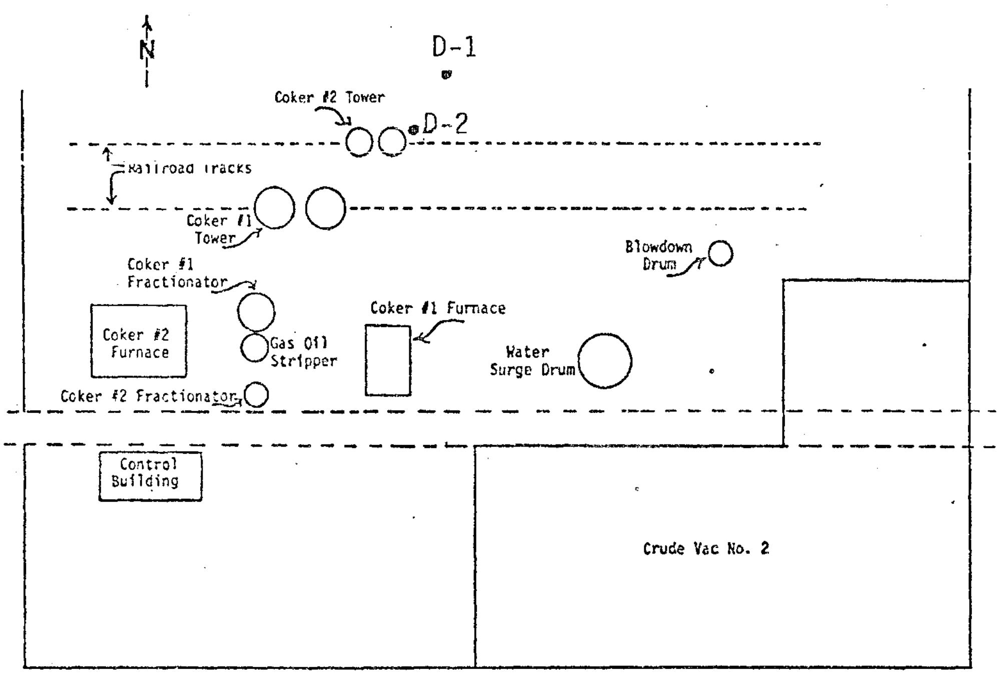

FIGURE IV-4. Delayed Coker Unit Area Sampling Locations

B. Personal Sampling

The two operational workers and all of the coke handlers (three on May 28, four on May 30) described in Chapter III, were sampled during both sampling shifts. During the first shift, a delayed start and several minor problems prevented sampling of the complete cutting operation. Sampling was terminated with about 1 hour of cutting remaining.

ASPHALT BLOWING UNIT

Locations A-1 and A-2 (Figure IV-5) were sampled on May 30. Location A-1 was on one of the two asphalt pumps that move the oxidized product from the towers to storage. This pump was in use about 3 hours of the shift. The sampling units were located about 3 feet above ground level. Location A-2 was a fire extinguisher post about 50 feet downwind from the towers and asphalt pumps and at the northeast corner of the unit. The sampling units were about 4 feet above ground level.

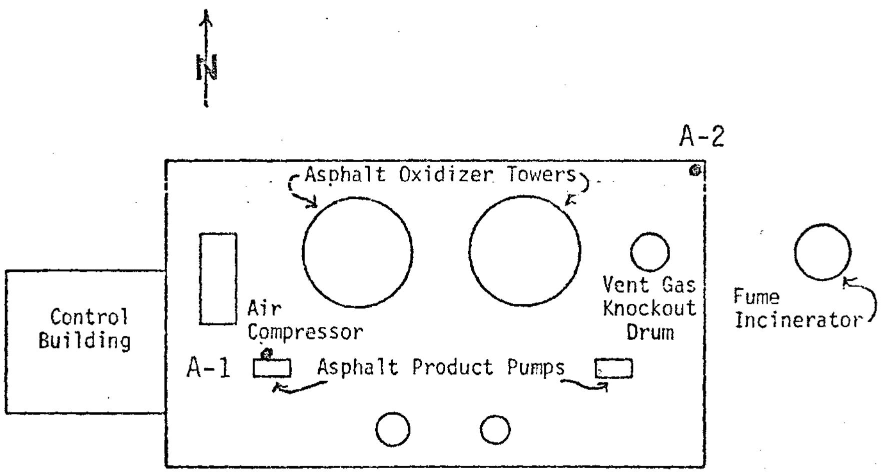

FIGURE IV-5. Asphalt Blowing Unit Area Sampling Locations

V. RESULTS AND DISCUSSION

The complete results of the area and personal PAH samples collected at this SOHIO refinery are presented in Tables V-1 and V-2. All 25 personal and area samples analyzed from the three study process units had detectable quantities of at least 7 of the 23 PAHs or groups of PAHs for which the samples were tested. The cumulative PAH concentrations for individual samples ranged from 1.6 $\mu g/m^3$ for a personal sample from one of the north-side operators to as high as 57.4 $\mu g/m^3$ for one location in the FCCU. The upwind boundary samples were 1.11 and 0.05 $\mu g/m^3$.

A summary of the personal and area sampling results, including the mean (arithmetic) cumulative PAH concentrations for the three process units and the northside operators, is presented in Table V-3. The north-side operators were the three operators who had responsibilities for the north side of the refinery production area which includes the FCCU, delayed coker, and several other process units. These three operators worked out of the main control building or nerve center. The table shows that the personal samples from the delayed coker unit were highest ($\overline{X}$ = 20.2 $\mu g/m^3$), followed by those from the north-side operators ($\overline{X}$ = 12.7 $\mu g/m^3$) and the FCCU ($\overline{X}$ = 5.4 $\mu g/m^3$). The means of the two area samples collected in the delayed coker unit and FCCU were quite similar (30.5 $\mu g/m^3$ and 27.0 $\mu g/m^3$) while the single area sample analyzed from the asphalt blower unit was less than one-tenth (2.1 $\mu g/m^3$) of the values at the other two units.

The distribution of individual PAHs by ring number generally showed that 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-ring and no 6- or 7-ring PAHs were found in the samples.

TABLE V-1. PAH Analytical Results (μg/m³) for Personal and Area Samples Collected at the FCCU, Asphalt, and Upwind Locations[a]

Ring No.	Sample Location:	AREA F-1	AREA F-2	FCC #1 OPERATOR		FCC #2 OPERATOR		NORTH INSIDE GENERAL OPER.		NORTH OUTSIDE GENERAL OPER.		NORTH OUTSIDE FOREMAN		ASPHALT A-1	UPWIND	
	Sample Date:	5/29	5/30	5/29	5/30	5/29	5/30	5/29	5/30	5/29	5/30	5/29	5/30	5/30	5/29	5/30
	Sample Volume (ℓ):	850	864	891	878	823	866	820	836	828	833	881	880	812	786	760
	Sample Time:	0721-1426	0709-1421	0653-1420	0757-1418	0650-1408	0659-1412	0705-1359	0654-1414	0700-1358	0651-1358	0658-1423	0647-1416	0745-1435	0733-1308	0758-1436
(2)	Naphthalene*	13.84	1.09	2.22	1.26	0.98	0.72	0.69	0.44	15.51	0.38	7.59	0.54	0.74	0.90	--[b]
(2)	Quinoline*	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
(2)	2-Methylnaphthalene	24.74	0.09	3.00	2.38	1.23	1.34	0.63	0.67	16.44	0.43	8.04	0.96	0.71	--	--
(2)	1-Methylnaphthalene	12.28	0.52	1.81	1.42	0.95	0.88	0.61	0.50	9.94	0.52	4.26	0.86	0.36	0.22	--
(2)	Acenaphthalene	0.74	--	0.04	--	--	--	--	--	--	--	0.12	--	--	--	--
(2)	Acenaphthene	1.53	0.12	0.09	0.25	0.15	0.13	0.03	0.28	0.44	--	0.40	0.15	--	--	--
(3)	Fluorene	1.05	0.15	0.06	0.24	0.13	0.18	0.13	0.35	0.31	--	0.40	0.18	0.10	--	--
(3)	Phenanthrene*/Anthracene*	2.90	0.40	0.58	0.77	0.37	0.36	0.40	0.81	0.62	0.26	1.11	0.77	0.11	--	0.05
(3)	Acridine	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
(3)	Carbazole	--	0.09	--	--	--	--	--	--	--	--	--	--	0.03	--	--
(4)	Fluoranthene	0.09	0.06	--	0.01	0.01	--	--	0.02	0.02	<0.01	0.05	<0.01	<0.01	--	--
(4)	Pyrene*	0.18	0.19	0.08	0.06	0.02	--	<0.01	0.04	0.02	<0.01	0.06	0.03	<0.01	--	--
(4)	Benzofluorene	0.02	0.03	--	--	--	--	--	--	--	--	--	--	--	--	--
(4)	Benz(a)anthracene*/ Chrysene*/Triphenylene	0.02	0.05	--	--	--	--	--	--	--	--	0.02	--	--	--	--
(5)	Benzo(e)pyrene*/ Benzo(a)pyrene*	--	--	0.02	<0.01	--	<0.01	<0.01	--	--	<0.01	<0.01	--	--	--	--
(5)	Perylene	--	--	--	<0.01	--	<0.01	<0.01	--	--	<0.01	<0.01	--	--	--	--
(5)	Dibenz(a,j)acridine*	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
(5)	Dibenz(a,i)carbazole*	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
(6)	Indeno(1,2,3-cd)pyrene*	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
(5)	Dibenzanthracene*[c]	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
(6)	Benzo(g,h,i)perylene	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
(7)	Coronene	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
(6)	Dibenzpyrene*[c]	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	TOTAL	57.39	3.60	7.90	6.39	3.84	3.61	2.68	3.11	43.30	1.59	22.05	3.49	2.05	1.11	0.05

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

TABLE V-2. PAH Analytical Results ($\mu g/m^3$) for Personal and Area Samples Collected at the Delayed Coker Unit[a]

Ring No.	Sample Location:	AREA		OPERATIONAL				COKE HANDLERS							
		D-1	D-2	Operator #1		Operator #2		Driller		Cleaner #2		Cleaner #3		Cleaner #4	
	Sample Date:	5/28	5/30	5/28	5/30	5/28	5/30	5/28	5/30	5/28	5/30	5/28	5/30	5/28	5/30
	Sample Volume (ℓ):	886	799	877	878	398	851	856	849	937	831	[b]	764	[c]	835
	Sample Time:	1540-2319	0734-1428	1447-2212	0650-1418	1505-2243	0652-1415	1525-2251	0710-1421	1512-2310	0715-1419		0750-1422		0718-1424
(2)	Naphthalene*	2.42	2.84	7.98	1.32	2.75	3.69	16.83	2.68	6.98	1.76		1.52		5.27
(2)	Quinoline*	--[d]	--	--	--	--	--	--	--	--	--		--		--
(2)	2-Methylnaphthalene	2.65	3.54	7.12	2.26	2.70	5.33	11.88	3.41	5.22	1.71		2.97		7.32
(2)	1-Methylnaphthalene	1.21	1.66	3.54	1.41	1.45	3.04	4.94	1.48	3.23	0.88		1.45		3.05
(2)	Acenaphthalene	0.16	--	0.33	0.13	0.17	0.31	0.46	0.16	--	0.08		0.20		0.36
(2)	Acenaphthene	0.37	0.38	0.58	0.40	0.38	--	0.92	--	0.69	0.16		0.18		0.71
(3)	Fluorene	0.51	0.34	0.79	0.35	0.44	0.55	1.51	0.30	0.73	0.21		0.67		0.91
(3)	Phenanthrene*/Anthracene*	11.20	2.75	4.12	1.72	2.26	2.71	14.86	1.86	6.81	1.45		4.35		5.55
(3)	Acridine	--	--	--	--	--	--	--	--	--	--		--		--
(3)	Carbazole	0.33	--	--	--	--	--	--	--	--	--		--		--
(4)	Fluoranthene	3.41	0.25	0.26	0.06	0.06	0.09	0.85	0.09	0.51	0.08		0.42		0.40
(4)	Pyrene*	12.45	0.72	0.83	0.23	0.20	0.32	2.65	0.35	1.85	0.30		1.39		1.23
(4)	Benzofluorene	--	--	--	--	--	--	--	<0.01	--	--		0.30		0.40
(4)	Benz(a)anthracene*/ Chrysene*/Triphenylene	5.62	0.23	0.25	0.02	0.01	0.03	0.53	0.05	0.61	0.17		1.63		1.22
(5)	Benzo(e)pyrene*/ Benzo(a)pyrene*	0.70	0.16	--	--	--	--	<0.01	--	--	0.06		0.76		0.57
(5)	Perylene	--	0.16	--	--	--	--	<0.01	--	--	--		0.04		--
(5)	Dibenz(a,j)acridine*	--	--	--	--	--	--	--	--	--	--		--		--
(5)	Dibenz(a,i)carbazole*	--	--	--	--	--	--	--	--	--	--		--		--
(6)	Indeno(1,2,3-cd)pyrene*	--	--	--	--	--	--	--	--	--	--		--		--
(5)	Dibenzanthracene*[e]	--	--	--	--	--	--	--	--	--	--		--		--
(6)	Benzo(g,h,i)perylene	--	--	--	--	--	--	--	--	--	--		--		--
(7)	Coronene	--	--	--	--	--	--	--	--	--	--		--		--
(6)	Dibenzpyrene*[e]	--	--	--	--	--	--	--	--	--	--		--		--
	TOTAL	41.03	13.03	25.80	7.90	10.42	16.07	55.43	10.38	26.63	6.86		15.88		26.83

* Suggested as having some cancer-causing potential.
[a] Blank values have been subtracted from data. Data have not been corrected for temperature and pressure variation; maximum deviation would be within ±2% of actual values.
[b] Sample lost.
[c] There is no Cleaner #4 during the evening shift.
[d] "--" designates compounds not detected.
[e] Specific isomers not distinguishable by analytical method; reported value represents any one or combination of existing isomers.

TABLE V-3. Summary of PAH Results

	PERSONAL SAMPLES			AREA SAMPLES		
	No. of Samples	$\overline{X}$ ($\mu g/m^3$)	No. of PAHs	No. of Samples	$\overline{X}$ ($\mu g/m^3$)	No. of PAHs
FCCU	4	5.4	8-10	2	30.5	11
Delayed Coker	10	20.2	9-13	2	27.0	11-12
North Side Oper.	6	12.7	8-12	--	--	--
Asphalt Blower	--	--	--	1	2.1	8
Total	20	15.0	8-13	5	23.4	8-12

FCCU

The average cumulative PAH concentration ($\overline{X}$) over the two shifts for the two FCCU workers was 5.4 $\mu g/m^3$ with the number of individual PAHs or groups of PAHs ranging from 8 to 10. Both of these workers are outside operators; there is no inside (board) operator specifically for the FCCU since the whole north production area is run out of the nerve center. Table V-4 shows that the FCC #1 operator was exposed at an average cumulative PAH concentration ($\overline{X}$ = 7.1 $\mu g/m^3$) higher than the FCC #2 operator ($\overline{X}$ = 3.7 $\mu g/m^3$). The FCC #1 operator was also exposed to a slightly larger number of individual PAHs (9-10 vs. 8). These results are consistent with the fact that the FCC #1 is responsible for the section of the unit (e.g., R/R, fractionator, slurry pumps) that is associated with the heavy-fraction streams while the FCC #2 is not.

TABLE V-4. Personal Monitoring Results — FCCU

	No. of Samples	$\overline{X}$ ($\mu g/m^3$)	No. of PAHs
FCC #1 Operator	2	7.1	9-10
FCC #2 Operator	2	3.7	8
Total	4	5.4	8-10

The results of the personal monitoring for the FCCU workers were quite consistent over the 2 days. There was less than 20% difference between the duplicate samples collected for both operators (Table V-1). 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; such an analysis will be included in the final summary report when data from all nine Phase III surveys are available.

The area sample (F-1) collected near the slurry recycle pumps showed a cumulative PAH concentration of 57.4 $\mu g/m^3$ with 11 PAHs identified; this PAH concentration was the highest of the samples collected at this refinery. Results for the other area sample, collected near the decanted oil pump, was 3.6 $\mu g/m^3$ with 11 PAHs identified.

DELAYED COKER UNIT

Table V-5 gives a summary of the personal monitoring results for the six coke workers. These values ($\overline{X}$) are again average cumulative PAH concentrations for the 2 sampling days. Table V-5 shows that the four coke handlers were exposed at higher concentrations than the two operational workers. Of the four coke handlers, the driller, who spends most of his shift in the enclosed penthouse, showed the highest cumulative PAH concentration ($\overline{X}$ = 32.9 $\mu g/m^3$). He was followed by cleaner #4 ($\overline{X}$ = 26.9 $\mu g/m^3$) who only works the day shift. Cleaner #2, who relieves the driller, was next ($\overline{X}$ = 18.5 $\mu g/m^3$) followed by cleaner #3 ($\overline{X}$ = 15.9 $\mu g/m^3$). Only one sample was collected for cleaner #3 due to equipment problems during the first sampling shift. The results for the two operational workers were quite similar ($\overline{X}$ = 16.9 and 13.2 $\mu g/m^3$; 10 and 9-10 PAHs).

TABLE V-5. Personal Monitoring Results — Delayed Coker Unit

	No. of Samples	$\bar{X}$ (μg/m³)	No. of PAHs
Operational	4	15.0	9-10
Operator #1	2	16.9	10
Operator #2	2	13.2	9-10
Coke Handlers	6	23.7	9-13
Driller	2	32.9	10-12
Cleaner #2	2	18.5	9-11
Cleaner #3	1	15.9	13
Cleaner #4	1	26.9	12
Total	10	20.2	9-13

The primary difference between the two sampling shifts at this unit was that needle coke was cut from coke tower #2 during the first sampling shift (evening shift) while sponge coke was cut from coke tower #1 during the second sampling shift (day shift). This difference is reflected in the cumulative PAH concentration results; unlike the sample results obtained from the FCCU, there was no consistency between the two sets of samples. The cumulative PAH concentrations were generally higher during the first shift when needle coke was cut. For the four coke workers sampled during both shifts (operator #1, operator #2, driller, cleaner #2), the mean cumulative PAH concentration for the first shift was 29.6 μg/m³ and 10.3 μg/m³ for the second shift.

The two area samples taken in the delayed coker unit showed cumulative PAH concentrations of 41.0 μg/m³ (12 PAHs identified) and 13.0 μg/m³ (11 PAHs); both were collected (one each shift) downwind of the drum being cut. The much higher sample was collected during the shift that needle coke was cut.

NORTH-SIDE OPERATORS

The mean cumulative PAH concentration over the two shifts for the three north-side operators was 12.7 μg/m³ with the number of individual PAHs ranging from 8 to 12. Table V-6 shows that the two outside operators (i.e., north outside general operator and north outside foreman) were exposed at much higher concentrations than the north inside general operator (17.6 μg/m^3 vs. 2.9 μg/m^3).

TABLE V-6. Personal Monitoring Results — North-Side Operators

	No. of Samples	$\overline{X}$ (μg/m^3)	No. of PAHs
Outside Operators	4	17.6	8-12
North Outside General Operator	2	22.4	8
North Outside Foreman	2	12.8	8-12
Inside Operator — North Inside General Operator	2	2.9	8-9
Total	6	12.7	8-12

The results for the inside operator were quite consistent over the 2 days, with less than a 15% difference in cumulative PAH concentrations; however, there was tremendous variation for the two north outside operators. The results for both workers were much higher on the first sampling day. The work schedules of these two operators vary more from day to day than do those of normal unit operators. Because they have responsibilities for a group of units, every day is usually different in terms of the amount of time spent in particular units. This can help explain the large variation in PAH levels between the 2 days. It was noted that the north outside general operator spent a large part of his shift during the second day near the cooling towers away from the FCCU and coker units, while he spent the first day more in the general production areas.

ASPHALT BLOWING UNIT

The area sample (A-1) collected on the asphalt product pump showed a cumulative PAH concentration of 2.1 μg/m^3 with eight PAHs identified. The second area sample collected at this unit was not analyzed because the sampling unit was broken during transport.

PAH DISTRIBUTION

Table V-7 shows the percent distribution of PAHs found at the three process units, for the north-side operators and at the upwind location. As the table indicates, the distribution is quite similar for all samples, except for those collected at the delayed coker unit. For the FCCU, asphalt blowing unit, upwind location, and the north-side operators, at least 88.3% of the PAHs found were the lighter molecular weight, 2-ring compounds. The PAH distribution found at the delayed coker showed much higher percentages of the 3-ring (26.3%) and 4-ring (15.6%) PAHs and, unlike the other units, some 5-ring compounds (1.0%) were detected. In all of the samples, naphthalene and its two methyl derivatives were generally found in the highest concentrations; in the delayed coker samples, the phenanthrene/anthracene group and pyrene were also found in relatively high concentrations.

TABLE V-7. Distribution (%) of PAHs Found by Ring Number

RING NO.	FCCU	DELAYED COKER	NORTH-SIDE OPERATORS	ASPHALT BLOWING	UPWIND
2	90.2	57.2	92.6	88.3	95.7
3	8.8	26.3	7.1	11.7	4.3
4	1.0	15.6	0.3	0	0
5	0	1.0	0	0	0
6	0	0	0	0	0
7	0	0	0	0	0

PARTICLE-SIZE DISTRIBUTION

Table V-8 shows the particle-size distribution of the six total particulate samples collected alongside the PAH area samples at the three study process units. The samples were consistent in that the great majority (at least 95.5%) of the particles sized were less than 6 µm and all (100%) were 11.8 µm or less. The two samples from the asphalt blowing unit showed that 99% of the particles were less than 3 µm. The two delayed coker samples and one from the FCCU showed a relatively higher distribution of larger particles.

TABLE V-8. Particle-Size Distribution (%) of Total Particulate Area Samples

PARTICLE SIZE (μm)	FCCU		DELAYED COKER		ASPHALT	
	F-1	F-2	D-1	D-2	A-1	A-2
0.4-0.7	53.9	35.9	38.9	27.4	55.8	54.3
0.7-1.0	27.9	30.1	29.1	33.2	33.3	31.4
1.0-1.5	13.2	12.3	20.9	18.7	5.0	7.2
1.5-2.1	2.5	7.1	1.6	6.8	2.6	4.9
2.1-2.9	2.5	4.9	4.6	2.3	2.6	1.3
2.9-4.2	0	2.6	2.0	2.9	0.3	0.7
4.2-5.9	0	4.2	1.3	4.2	0.3	0
5.9-8.3	0	2.3	1.0	1.9	0	0.3
8.3-11.8	0	0.7	0.7	2.6	0	0

VI. CONCLUSIONS

The results of the personal, area, and upwind air samples from the SOHIO refinery clearly indicate that workers at the FCCU and delayed coker unit of this refinery and the north-side operators are exposed to numerous PAHs, generally at low $\mu g/m^3$ concentrations. Only one area sample was analyzed from the asphalt blowing unit; where 8 PAHs were identified compared to background levels of 2 PAHs (upwind samples), the data tend to indicate that workers were exposed to PAHs at this unit. In attempting to draw conclusions from this survey, one must keep in mind that the samples were collected over only three work shifts. 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 personal sampling results indicate that the operators at the delayed coker unit were exposed at the highest PAH concentrations, followed by the north-side operators and the FCCU operators, in that order. At the delayed coker unit, the four coke handlers were exposed at higher concentrations than the two operational workers. Of the coke handlers, the driller, who spent most of his shift in the enclosed penthouse, showed the highest results. As anticipated, the two north outside operators were exposed at much higher concentrations than the north inside operator. However, this inside operator, who spent essentially 100% of his shift inside the nerve center, was exposed to a variety of different PAHs at levels comparable to those to which the FCCU operators were exposed. The FCCU personal samples showed that the operator assigned to the FCC #1 area was exposed to higher PAH concentrations and more PAHs than the operator assigned to the FCC #2 area. This had been anticipated since the process streams containing the heavy petroleum fractions are mainly confined to the FCC #1 area of the unit.

At the FCCU, the personal sampling data were quite similar over the two sampling shifts; for the delayed coker unit and the north-side operators, the concentrations were generally higher during the first sampling shift. At the delayed coker unit, the primary difference noted between the two shifts was that needle type coke was cut the first day and sponge type was cut the second day. The wide variations for the two outside north operators can best be explained by the fact that their duties and work locations vary greatly from day to day depending on specific work assignments or problem areas.

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, in order to check suspected major PAH emission sources and to compare concentrations and PAH distributions with the personal samples. It was anticipated that the area samples would be considerably higher than the personal samples. This was the case at one sampling location at each of the two units. At the FCCU, the sample collected at the slurry recycle pump yielded the highest cumulative PAH concentration of any sample collected at this refinery. This indicates that the slurry recycle pump area is a source of PAH emissions. In the delayed coker unit, both area samples (one each shift) were collected downwind of the cutting operation. The results of the sample collected during the first shift was considerably higher than the second-day sample; this was consistent with the trend noted in the personal samples showing high levels during the cutting of needle coke. The results showed that there was not a tremendous difference between the area and personal samples and that PAH levels were found for those workers who do not work in high PAH emission areas (i.e., north-side inside general operator, FCC #2 operator), indicating that PAHs are not restricted to the areas around major emission sources but are probably widespread throughout many areas of these units.

As expected from Phase II results, a great proportion of the PAHs identified were the lighter 2- and 3-ring compounds. The delayed coker samples were noticeably different from the other samples in that there were larger percentages of the 3-, 4-, and 5-ring PAHs.

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

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

APPENDIX

Attendees of Opening Conferences

Enviro Control, Inc.

Stan Futagaki	Senior Industrial Hygienist
Robert Reisdorf	Industrial Hygienist

Standard Oil of Ohio

C. M. Tyler	Manager of Toledo Refinery
E. M. Smith, Jr.	Employee Relations Manager
G. L. Perlinsh	Union/Management Safety Committee
J. B. Huskisson	Safety Director
B. P. Sumner	Health and Safety
A. L. Lott	Corporate Industrial Hygienist