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HEALTH HAZARD EVALUATION REPORT

HETA 94-0253-2451
PAN AMERICAN HEALTH ORGANIZATION
BOGOTA, COLOMBIA, SOUTH AMERICA

HETA 94-0253-2451 NIOSH INVESTIGATORS:
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I. SUMMARY

At the request of the Pan American Health Organization (PAHO), the National Institute for Occupational Safety and Health (NIOSH) conducted an industrial hygiene survey at the ECOPETROL Oil Refinery in Barrancabermeja, Colombia, to measure workers' exposures to benzene, toluene, xylene, ethyl benzene, and cyclohexane.

From May 17 to May 21, 1994, 72 personal breathing zone and 45 area samples were collected. Personal exposures and area measurements for toluene (<minimum detectable concentration [MDC] - 18 parts per million [ppm]), xylene (<MDC - 5 ppm), ethyl benzene (<MDC - 1 ppm), and cyclohexane (<MDC - 14 ppm), were well below the NIOSH recommended exposure limits (RELs). Full-shift exposures to benzene for maintenance personnel, laborers, and operators working in the aromatics plant, ranged from less than the MDC to 32 ppm. The median full-shift exposure for maintenance personnel was 6 ppm, which is above the NIOSH REL of 0.1 ppm and also above the permissible exposure limit (PEL) of 1 ppm set by the Occupational Safety and Health Administration (OSHA). Operators' median exposure was 0.2 ppm which is also above the NIOSH REL. The median short-duration exposure to benzene for maintenance personnel was 5.2 ppm which is above the NIOSH short-term exposure limit (STEL) of 1 ppm, and the OSHA STEL of 5 ppm.

Measurements made in the aromatics plant identified several areas where workers could be exposed to benzene at levels above the REL if

Full-shift and short-duration benzene exposures for some employees were above the NIOSH and OSHA exposure levels. These results indicate that a hazard exists for some ECOPETROL employees from overexposures to benzene. Recommendations for controlling exposures to benzene, including the use of personal protective equipment and the implementation of an environmental monitoring program, are provided in section VIII of this report.

they spent considerable amounts of time in those areas. One area in the gas chromatography laboratory was also identified as a potential source of significant benzene exposures.

KEYWORDS: SIC 2911 (petroleum refining), oil refinery, aromatic hydrocarbons, benzene

II. INTRODUCTION

In a letter dated March 18, 1994, the Pan American Health Organization (PAHO) requested assistance from the National Institute for Occupational Safety and Health (NIOSH) in conducting a pilot study at the ECOPETROL Oil Refinery in Barrancabermeja, Colombia. The purpose of this study was to evaluate employees' exposures to benzene, toluene, xylene, ethyl benzene, and cyclohexane in various areas of the refinery.
The goals from this evaluation were: (1) to determine if workers' current exposures to these chemicals represented a health hazard, and (2) to provide information for an epidemiology study of neurobehavioral health effects and hydrocarbon exposures that PAHO is conducting at the request of ECOPETROL management and the Union, Union Sindical Obrero (USO).

NIOSH investigators conducted a field survey at the refinery from May 16 to May 21. During this survey, environmental samples were collected to measure personal exposures and area concentrations of these compounds in the aromatics plant, the quality control (QC) laboratory, and the shipping department. PAHO investigators had previously identified these as potentially high-exposure areas. (The alkylation and paraffin plants were also identified as potentially high-exposures areas, but these plants were not operating during the survey period. Therefore, samples were not collected there.) Environmental samples were also collected in the warehouse, health clinic, and administrative office. Personnel from these areas were being considered for use as controls in the epidemiology study.

III. BACKGROUND

ECOPETROL is an integrated oil refinery located on the east bank of the Magdalena River. It has a refining capacity of 200,000 barrels per day. In the aromatics plant, benzene, toluene, xylene, ethyl benzene, and cyclohexane are refined from naphtha. This process is monitored by operators from inside a control room. Operators make rounds several times during their shift to monitor process parameters, collect QC samples, and inspect the system. Different operators are responsible for different areas of the plant. Equipment in the aromatics plant includes furnaces, heat exchangers, pumps, tanks, fractionating columns, pipes, pipe fittings, and valves. Plant equipment is serviced by a maintenance crew assigned to the aromatics and alkylation plant. QC samples, collected in the aromatic plant and other production plants, are analyzed in the QC laboratory. Laboratory personnel use various analytical methods to check the quality of in-process and finished products. Finished products are shipped from the refinery to customers via barges or tank truck. Personnel in the shipping department supervise the transfer of the finished product from storage tanks into the barges and tankers, and monitor tank levels. Personnel in the warehouse receive and stock the parts necessary for refinery operations. The health clinic, staffed by ECOPETROL health care workers, provides basic health care for ECOPETROL employees and their families.

ECOPETROL personnel who were monitored worked one of two shift patterns. They either worked eight continuous hours, taking a ½-hour lunch break, or they worked 4½ hours, took a 1½ hour lunch break, and then returned to work for 4½ hours. One exception to these patterns is the tank filler who transfers finished product into tank trucks. He reported that he leaves whenever the last tanker of the day has been filled, resulting in a workshift duration of five to eight hours.

IV. EVALUATION CRITERIA

A. Environmental criteria

General

In evaluating the hazards posed by workplace exposures to chemical and physical agents, NIOSH field staff use various environmental evaluation criteria. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to ten hours per day, 40 hours per week, for a working lifetime without experiencing adverse health effects. However, the criterion may not protect workers who are more susceptible to the exposure agent, such as those with a pre-existing medical condition. Furthermore, these criteria generally do not account for the combined effects that some hazardous substances have with other factors, such as other workplace exposures, ambient or residential exposures, medications, or personal habits of the worker. Also, these criteria generally do not account for multiple exposure routes. For example, in addition to inhalation exposures of chemical agents, the exposure route for which most criteria are developed, some compounds are absorbed by direct contact with the skin and mucous membranes, which can increase the overall exposure. Finally, evaluation criteria may not reflect what is currently known about the exposure agent. This can occur either because the toxicity information used to develop the current criterion is outdated, or because of the lag time between the availability of new information and the adoption of new criteria.

The primary sources of environmental evaluation criteria for workplaces in the United States are: (1) NIOSH Criteria Documents and

Recommended Exposure Limits (RELs),[1] (2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs),[2] and (3) the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs) for general industry.[3] The OSHA exposure limits may be required to take into account the feasibility of controlling exposures in various industries where the agents are used, while the NIOSH-recommended exposure limits are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that employers in the United States are legally required to comply with OSHA standards and meet those levels specified by OSHA PELs.

The NIOSH RELs, OSHA PELs, and ACGIH TLVs are time-weighted averages (TWAs). A TWA exposure refers to the average airborne concentration of a substance over a defined period of time. An 8- to 10-hour TWA refers to the airborne concentration of substance measured during a normal workshift. Some substances have recommended short-term exposure limits (STELs) or ceiling values (C) which are intended to supplement the TWA exposure limit where there are recognized toxic effects from high, short-term exposures. A STEL is defined as a 15-minute TWA exposure limit which should not be exceeded at any time during the workshift even if the 8-hour TWA exposure is within the established criterion. Ceiling values are concentrations which should not be exceeded at any time during the work shift.

In comparing the air sampling results to the exposure criteria, the reader should be aware that the criteria are intended to be used as general guidelines and do not define an exact level of safety. Also remember that environmental monitoring was conducted over a relatively short period of time and that workers' exposures are likely to vary. The results obtained in a short-term evaluation of this type should not be considered definitive. In general, exposure measurements which approach or exceed exposure criteria indicate the need for improved controls and further evaluation.

B. Benzene

Acute benzene overexposure can cause central nervous system (CNS) depression with symptoms such as headache, nausea, and drowsiness. Chronic exposure to benzene has been associated with the depression of the hematopoietic (blood-forming) system and is associated with an increased incidence of leukemia and possibly multiple myeloma.[4] The NIOSH REL is 0.1 parts per million (ppm). NIOSH further recommends a 15-minute STEL of 1.0 ppm. Although NIOSH has established these guidelines which should not be exceeded, the Institute urges that exposures be reduced to the "lowest feasible level" (LFL) because it is not possible to establish thresholds for carcinogens which will protect 100% of the population. OSHA also considers benzene to be a carcinogen, and has promulgated a PEL of 1 ppm and a STEL of 5 ppm. The current ACGIH TLV is 10 ppm, and ACGIH has classified benzene as a suspected human carcinogen. Since 1990, ACGIH has proposed to lower the TLV for benzene to 0.1 ppm, and since 1991, to classify it as a confirmed human carcinogen, but this has yet to be adopted by the ACGIH TLV committee.

C. Toluene

Overexposure to toluene can cause irritation of the eyes, respiratory tract, and skin; CNS depression; and neurotoxicity.[5] Since it is a defatting solvent, repeated or prolonged skin contact will remove the natural lipids from the skin which can cause drying, fissuring, and dermatitis.[6] The NIOSH REL for toluene is 100 ppm. NIOSH further recommends a STEL of 150 ppm. The OSHA PEL for toluene is 200 ppm. The ACGIH TLV is 50 ppm. The ACGIH TLV also carries a skin notation, indicating that the cutaneous route of exposure may contribute significantly to the overall exposure.

D. Xylene

Overexposure to xylene can cause irritation of the eyes, respiratory tract, and skin; CNS depression; and neurotoxicity. Repeated or prolonged skin contact may cause erythema, drying, and defatting of the skin which may lead to the formation of small blisters.[7] The NIOSH REL, OSHA PEL, and ACGIH TLV for xylene are 100 ppm. NIOSH further recommends a STEL of 150 ppm.

E. Ethyl Benzene

Overexposures to ethyl benzene can cause irritation of the eyes, respiratory tract, and skin, and may also cause narcosis in humans.[5] The NIOSH REL, OSHA PEL, and ACGIH TLV for ethyl benzene are 100 ppm. NIOSH and ACGIH further recommend a STEL of 125 ppm.

F. Cyclohexane

Overexposures to cyclohexane can cause irritation of the eyes, respiratory tract, and skin, and may also cause narcosis in humans.[5] The NIOSH REL, OSHA PEL, and ACGIH TLV for cyclohexane are 300 ppm.

V. METHODS

A total of 72 personal breathing zone (PBZ) and 45 area samples were collected according to NIOSH Method 1501,[8] with three modifications. First, the tubes used to collect most of the samples were Anasorb® 747 (SKC catalog # 226-83).[9] We chose these tubes because the adsorption media they contain, a synthetic carbon, is less hygroscopic than charcoal. Therefore, their adsorption capacity for hydrocarbons is thought to be less affected by high humidity levels which were of concern at this workplace. Second, charcoal tubes (SKC catalog # 226-09) were used for ten of the PBZ samples and two of the area samples to compare their performance to the Anasorb® tubes. (These charcoal samples, most of which were collected using a two-tube manifold, are indicated in Table 1 with a "b" or an asterisk [*] in the sample number column.) Both the Anasorb® and charcoal tubes contain 400 milligrams (mg) of media in their front section and 200 mg of media in their back-up section. These larger tubes were used because we were concerned that the high humidity and temperature levels in Barrancabermeja would significantly reduce the adsorption capacity of the media. Third, also due to this concern, we placed 150 mg charcoal tubes (SKC catalog # 226-01) in series behind the larger tubes.

A flow rate of 50 cubic centimeters per minute (cc/min) was used to collect most full-shift personal and area samples. In general, a flow rate of 200 cc/min was used for shorter-duration samples, of which there were 16 PBZ and 19 area. The pumps were calibrated before and after each sampling period using a Gillian Gillibrator equipped with a 20 to 6000 cc/min flow cell (part # D800286). The flow rates, durations, and air volumes for each sample are provided in Table 1.

The job titles of those employees who were monitored are provided in Table 1 (most of these job titles were provided by the employees). The locations where area samples were collected from are also listed in Table 1. Most areas in the aromatics plant correspond to letter-number designations found on equipment near the sample location.

The pumps worn by employees working eight continuous hours were allowed to operate during the employees' lunch period. In general, those pumps worn by employees who took a 1½ hour lunch break were collected and turned off, and the sample tubes were capped during their lunch breaks. When these workers returned, each pump was replaced back on the same worker who had worn it before the break, the tubes were uncapped, and the pumps turned back on.

On May 17, 21 PBZ and 9 area samples were collected in the aromatics plant. All but one of the employees monitored were operators. The remaining employee was a laborer who was cleaning various equipment in the aromatics plant. On May 18, 10 PBZ and 7 area samples were collected in the warehouse. Also on May 18, one PBZ and one area sample were collected at the shipping platform where the tank trucks are loaded, and one short-duration sample was collected from a pumphouse operator while he measured tank levels. On May 19, eight full-shift and four short-duration PBZ samples were collected from employees who simulated the repair of a benzene pump in the aromatics plant from 7:00 a.m. to 9:00 a.m. The pump was not in need of repair, but was removed and reinstalled at the request of PAHO personnel in order to monitor exposures during this task. Four PBZ samples were also collected on insulators working in the alkylation plant, and one area sample was collected in the control room of the alkylation plant. One PBZ and one area sample were collected at the shipping platform where the tank trucks are loaded and an additional PBZ sample was collected from one of the pumphouse operators. One PBZ sample was also collected from a worker in the laundry facility, where the clothing of employees from the aromatics and alkylation plant was washed. On May 20, 14 PBZ and 5 area samples were collected in the laboratory, and 3 area samples were collected in the health clinic. On May 21, 9 short-duration PBZ and 17 area samples were collected in the aromatics plant. Also on May 21, one area sample was collected in the control room of the alkylation plant, and two area samples were collected from the administration offices, one in the personnel office and one outside the office of the superintendent of crude refining. All samples, with the exception of nine PBZ samples collected on May 17 during the afternoon shift, were collected during the first workshift (6:00 a.m. to 2:00 p.m.).

The samples were analyzed by gas chromatography (GC) according to NIOSH Method 1501 with three modifications.

First, desorption was performed using 2.0 milliliters (ml) of carbon disulfide (CS_2) that contained 1 microliter per milliliter (µl/ml) of decane as an internal standard. Second, the column used was a 30 meter by 0.32 millimeter fused silica capillary column coated internally with 0.25 micrometers of DB-1. Third, the column temperature was programmed to hold at 30°C for the initial 12 minutes of the analysis run, and then increase to a final temperature of 200°C at a rate of 20°C per minute. The limit of detection (LOD) reported by Datachem Laboratories (the laboratory contracted by NIOSH) was either 0.001 or 0.002 milligrams per sample (mg/sample) for benzene, and 0.01 mg/sample for toluene, xylene, ethyl benzene, and cyclohexane. The limit of quantitation (LOQ) reported was either 0.0033 or 0.0039 mg/sample for benzene, and 0.033 mg/sample for toluene, xylene, ethyl benzene, and cyclohexane. Following analysis of the front tubes, a set of 22 back-up tubes were analyzed to test for breakthrough. The tubes chosen corresponded to samples which had the highest concentrations of analytes on the front tubes.

Five quality control samples were submitted for analysis with the sample set. Onto each of these samples, 0.181 mg of toluene and 0.0606 mg of xylene were injected.

Temperature and relative humidity measurements were made using a battery-operated psychron (Environmental Tectonics Corporation Psychro-Dyne). Measurements were made at least once in the morning and once in the afternoon daily.

VI. RESULTS

Toluene, Xylene, Ethyl Benzene, and Cyclohexane

The results of the personal and area samples are provided in Table 1. Most of the personal exposures and area measurements for toluene, xylene, ethyl benzene, and cyclohexane were below the minimum detectable concentration (MDC). All exposures to these analytes were well below the NIOSH exposure limits. The highest full-shift exposure to toluene was 13.2 ppm (sample PBZ-14), the highest short-duration exposure to toluene was 2.9 ppm (PBZ-123), and the highest area concentration of toluene measured was 18.4 ppm (AREA-61). The highest full-shift exposure to xylene was 5.1 ppm (PBZ-82), all short-duration exposures to xylene were below the minimum quantifiable concentration (MQC), and the highest area concentration of xylene measured was 2.6 ppm (AREA-5). The highest full-shift exposure to ethyl benzene was 1.1 ppm (PBZ-82), all short-duration exposures to ethyl benzene were below the MQC, and the highest area concentration of ethyl benzene measured was 0.6 ppm (AREA-5). The highest full-shift exposure to cyclohexane was 0.7 ppm (PBZ-82), the highest short-duration exposure to cyclohexane was 13.6 ppm (PBZ-122), and the highest area concentration of cyclohexane was 2.7 ppm (AREA-134).

Benzene

Personal exposures and area measurements to benzene are summarized in Table 2, in which the results are categorized by sample location, job classification, and sample type. Included in each category of Table 2 is the number of samples, the range of sample durations, the minimum and maximum measurements, and where appropriate, the arithmetic mean and median. For side by side samples, only the Anasorb results were included in calculating the values in Table 2.

Maintenance employees in the aromatics plant who simulated the repair of the benzene pump had the highest median exposures. Their median full-shift exposure, based on 4 samples of durations ranging from 5 to 8 hours, was 6.1 ppm. Their median exposures during the task of pump "repair," based on 3 samples of 2 hours duration each, was 5.2 ppm. These levels are above the NIOSH REL and STEL, and also above the OSHA PEL and STEL. The employee with the highest personal exposure was also a maintenance worker, with an 8-hour TWA of 32 ppm. Those with the next highest exposures were the two laborers who had helped with the pump repair simulation. The laborers full-shift exposures were 0.40 and 0.67 ppm for sample durations of 7 and 8 hours. These values are above the NIOSH REL of 0.1 ppm. The short-duration exposure of the operator who had assisted in the repair simulation was 0.47 ppm for a sample duration of 2 hours. During the repair simulation, all personnel involved with this task wore quarter-mask air purifying respirators (APRs), hard hats, and steel-toed leather boots. Two workers wore safety glasses with side-shields, and one worker wore leather gloves.

Personal exposures to benzene for operators in the aromatic plant were also above the NIOSH REL. Their median full-shift exposures, based on 19 samples of durations ranging from 3 to 6 hours, was 0.21 ppm. Their median short-duration exposures, based on nine samples of durations between 15 and 30 minutes, was 0.66 ppm. This value is below the NIOSH STEL, however, exposures from two of the samples, 4.2 ppm and 2.3 ppm, were above the NIOSH STEL. During collection of the first sample (PBZ-123), the operator checked a tank level in the tank farm (K-1402, "sulfolane®"), and added oil to pump 1705-A. During collection of the second sample (PBZ-128), the operator collected nine QC samples, including two benzene samples from measuring station M-1500-02.
Some operators wore APRs during their rounds whereas others did not. The operator from

whom samples PBZ-123 and -128 were collected wore an organic-vapor (OV) APR during his rounds.

Personal exposures to benzene for employees in the shipping department varied. The exposure from one 2-hour sample collected on May 18 from the tank loader was 0.12 ppm, but his exposure from a 4.5 hour sample collected the next day was only 0.02 ppm. On May 18, two loads of xylene (8,800 gallons), one load of toluene (3,350 gallons), and one load of ethyl benzene (12,000 gallons) were transferred into tank trucks during the monitoring period. On May 19, three loads of ortho-xylene (29,100 gallons), nine loads of toluene (49,200 gallons), seven loads of mixed xylene (37,900 gallons), one load of cyclohexane (2,000 gallons), and one load of heavy aromatics (10,000 gallons), were transferred into tank trucks during the monitoring period. This employee reported that he wore his respirator, a quarter-mask APR with an OV and dust/mist cartridge (TC 23C-343/344/799), when he operated nozzles to fill the trucks. Both the short-duration and full-shift exposures of the pumphouse operator were below the MQC.

Personal exposures to benzene in the laboratory were below NIOSH exposure limits except for one charcoal tube sample (PBZ-b), which was 0.15 ppm; the result from the corresponding Anasorb® sample was below the MQC. One area measurement made in the GC laboratory near the work stations in the center of the room, was 0.87 ppm.

The personal exposure of the one laundry worker sampled was 0.03 ppm. Personal exposures of the two maintenance employees who were insulating equipment in the alkylation plant were below the MDC. Personal exposures and area measurements in the warehouse, health clinic, and administration building were also below the MDC.

In general, no problems were observed with the method used to collect and analyze the samples. Only one tube had a measurable amount of analyte on the back-up section of the tube, and that amount equaled 0.1% of the amount on the front section. Twenty micrograms of benzene were measured on the back-up tube from one sample (PBZ-73). This is 22% of the mass measured on the front tube. Analytes were not detected on the remaining 21 back-up tubes that were analyzed. The average percent recovery of toluene from the QC samples was 104%, with a range of 99% to 110%. (A value of 100% represents a recovery equal to that which was injected onto the tube.) The average recovery of xylene was 97% with a range from 96% to 101%.

There were two samples, PBZ-11 and PBZ-101, for which the results from side by side sampling of Anasorb and charcoal tubes differed. From sample PBZ-11, the benzene exposure measured was 0.12 ppm for the charcoal tube, whereas the exposure measured from the Anasorb tube was below the MDC. From sample PBZ-101, the benzene exposure measured was 0.15 ppm for the charcoal tube, whereas the exposure measured from the Anasorb tube was below the MQC.

Temperatures ranged from 21 to 36°C and percent relative humidities (%RH) ranged from 46 to 92%. The results, date, time, and location of each measurement are provided in Table 3.

VII. DISCUSSION

This investigation should not be considered a thorough evaluation of workers' exposures. Except for the aromatics plant and the shipping department, only one day's samples were collected from the areas investigated. Furthermore, many PBZ samples were less than 8 hours in duration. Because of these limitations, caution must be used in interpreting the results of this investigation.

The short-duration exposures of the maintenance workers to benzene indicate that there is a potential for them to be overexposed during pump repair. Also, the fact that the full-shift exposures for two of the maintenance workers were above their short-duration exposures, indicates that these workers had benzene exposures on May 19 in addition to those during the simulated pump repair.

Two work practices were observed during the simulated pump repair which likely contributed to workers' exposures. First, when the pump was disconnected from the system, liquid leaked onto the cement pad, resulting in a spill area of approximately eight square feet. Although it was not analyzed, this liquid was presumed to have been benzene. If it was benzene, this spill was a source of benzene exposures which could be avoided during future pump repair by either preventing the spill, or cleaning it up immediately. Second, except when the pump was raised with a hoist, only one or two employees worked on the pump at any one time. Despite this, all four of the maintenance personnel and both of laborers remained in the immediate area of the pump for the duration of the task, each being exposed to additional benzene vapors unnecessarily.

During the simulated pump change, workers wore APRs. Six potential problems with the workers' use of these respirators were identified. First, benzene does not have adequate warning properties to use cartridge respirators. Odor and irritation thresholds reported in the literature are above the NIOSH and OSHA exposure limits.[10,11] Second, at least one individual's respirator was equipped with a hydrogen sulfide and acid gas cartridge (NIOSH-approval number TC-23C-339), which will not protect against organic vapors. Third, even with organic vapor cartridges, the APRs used carry a NIOSH-assigned protection factor (APF) of only five. A fivefold reduction in exposures would not have reduced the full-shift or short-duration exposures of the maintenance personnel to below the respective NIOSH exposure standards. Fourth, the APRs used had a single strap which is designed to run behind the neck, attach to the respirator facepiece, and then run behind the head. The strap of one worker's respirator was broken, leaving a single non-adjustable strap behind the neck which had been tied to the facepiece. The strap of another respirator was twisted, with both sections running behind the neck. If the straps are not used correctly, an effective seal between the wearer's face and the facepiece of the respirator might not be obtained. Fifth, several respirators were worn with cloth liners. The use of a cloth liner will interfere with the seal between the face and mask, reducing the effectiveness of the respirator. This practice also invalidates the NIOSH certification of the respirator. Sixth, at least one of the cartridges used was only approved for half-mask models. Using these cartridges in quarter-mask models also invalidates the certification of the respirator.

During equipment maintenance in an oil refinery, there is a potential for dermal exposures to hydrocarbons. During the simulated pump repair, none of the employees wore gloves made of a material considered to be protective against hydrocarbons. One worker wore leather gloves, but this practice could actually increase exposures if the gloves became soaked. Examples of materials that are resistant to penetration by hydrocarbons are polyvinyl-alcohol or Viton™. Also, none of these employees wore splash-proof eye protection to prevent eye exposures from incidental contact such as from a splash or from rubbing the eye with a contaminated hand.

The operators in the aromatics plant spent most of their shift inside the control room, where concentrations to benzene averaged 0.07 ppm (samples AREA-1 through AREA-3). In addition, these workers received short-duration exposures while they made their rounds, as evidenced by the results from samples PBZ-121 through PBZ-129, which averaged 0.66 ppm. During rounds, particularly during the collection of QC samples, there is a potential for workers' eyes and hands to come in contact hydrocarbons. However, none of the operators were observed wearing splash-proof eye protection or chemically resistant gloves while making their rounds.

By protecting maintenance personnel, laborers, and operators from exposures during the relatively short time periods spent making repairs or rounds, it may also be possible to achieve full-shift exposures below the NIOSH REL. One method for controlling these exposures is through the use of respirators. However, respirators should only be used if they are part of a complete respiratory protection program. A list of ten items required by OSHA (29 CFR 1910.134)[12] as part of a respiratory protection program are attached at the end of this report. Further information about respirators and their use is provided in the NIOSH guide to respiratory protection.[13]

NIOSH recommends that only two types of respirators be used for reducing benzene exposures, either a full-face self-contained-breathing-apparatus (SCBA) or a Type C supplied-air respirator.[12] OSHA states that APRs can be used to protect against benzene exposures, but because of benzene's poor warning properties new cartridges must be installed at the beginning of each shift since currently-available cartridges are not equipped with an end-of-service-life indicator for benzene.[14] Tight-fitting full facepiece APRs equipped with the appropriate cartridge have an APF of 50, whereas the APF for a half-mask respirator is 10. Only 1 measurement, PBZ-14, was greater than 50 times the NIOSH REL. In contrast, 10 measurements were greater than 10 times the appropriate NIOSH exposure limit (either the REL or STEL). In addition to better protection against inhaling benzene vapors, full facepiece respirators also provide eye protection from incidental contact with liquid and gaseous forms of chemicals.

Results of the area measurements made in the GC laboratory suggest that there is a potential for exposures to benzene above the REL, particularly for those workers who spend much of their day at the work stations where the sample was collected. Furthermore, there is a potential for laboratory workers' eyes and hands to come in contact with benzene and other chemicals during analysis procedures.

The difference in exposures measured from side-by-side sampling using the Anasorb® and charcoal tubes for samples PBZ-11 and -101 was probably due to pump malfunction. The same pump was used to collect both samples. On three occasions, we were unable to post-calibrate the pump immediately following sample collection because the pump battery was drained of power. Instead, we calibrated the pump on the following morning after it had recharged. It is unlikely that the exposures truly differed because these samples were collected using a two-tube manifold, with the air inlets of the two tubes being separated by only 1.25 inches.

We cannot be certain of the source of the benzene measured on the back-up tube of sample PBZ-73. However, benzene was not detected on the back section of the front tube for this sample. This suggests that the back-up tube may have been contaminated during sample collection, shipping, or analysis.

VIII. RECOMMENDATIONS

(1) ECOPETROL should investigate methods for reducing the benzene exposures of maintenance personnel and laborers during the repair of benzene pumps or performance of other tasks which are likely to result in exposures that are above the NIOSH exposure limits. As an interim means of control, employees should wear full facepiece respirators while performing these tasks. If APRs are used, new cartridges should be installed at the beginning of each shift. If the maintenance task is likely to result in skin exposures to chemicals, workers should wear protective clothing that is made of a material which is resistant to penetration by those chemicals.

(2) To control their exposures to benzene, operators in the aromatics plant should wear full facepiece respirators while making their rounds. If APRs are used, new cartridges should be installed at the beginning of each shift. During the collection of QC samples, operators should wear gloves made of a material that is resistant to penetration by hydrocarbons.

(3) A complete respirator program, consistent with OSHA requirements (29 CFR 1910.134), should be implemented.

(4) Personal exposures to benzene in the GC laboratory should be further evaluated to determine if benzene exposures are above the NIOSH REL.

(5) An environmental monitoring program designed to accurately determine workers' exposures to solvents and other chemical and physical agents, should be implemented at ECOPETROL. Information concerning sampling strategies and other aspects of an environmental monitoring program is provided in the NIOSH publication: Occupational Exposure Sampling Strategy Manual,[15] and the ACGIH publication: Air Sampling Instruments for Evaluation of Atmospheric Contaminants, 7th ed.[16]

(6) NIOSH Method 1501, modified to use Anasorb 747 tubes, appears to be a good method for performing future environmental monitoring of benzene, toluene, xylene, ethyl benzene, and cyclohexane. This modification provides an increased capacity for adsorbing hydrocarbon vapors, while maintaining adequate sensitivity; the use of back-up tubes does not appear to be necessary.

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Attachment 1
Ten Items of a Respiratory Protection Program
HETA 94-0253
5/17/94 - 5/21/94

The Occupational Safety and Health Administration's General Industrial Standard on respiratory protection, 29 CFR 1910.134, which also applies to construction industry, requires that a respiratory protection program be established by the employer and that appropriate respirators be provided and be effective when such equipment is necessary to protect the health of the employee. They should be used as a primary control for employee protection only where engineering controls are not feasible or are currently being installed. The standard requires the employer to address ten basic requirements which would provide for an acceptable respiratory protection program. These requirements are summarized below for easy reference:

I. **Provide Written Operating Procedures**

The employer must prepare written standard operating procedures governing the selection and use of respirators. The procedures must include a discussion or explanation of all items specified in 29 CFR 1910.134(b).

II. **Proper Selection of Respirator**

The proper selection of a suitable respirator is dependant upon a number of parameters including: physical nature of the contaminant, concentration of contaminant in the air, toxicity of contaminant and warning properties of the substance (e.g., odor or irritation, which can indicate the end of the service life of the respirator).

III. **Training and Fitting for the Employee**

Requires that the user be instructed and trained in the proper use of respirators and their limitations, as well as with their maintenance. Qualitative fit testing of respirators fit in a test atmosphere is required. Some OSHA standards now require quantitative fit testing before assignment of a respirator to any employee. In addition, the employee shall be familiar with personal face fit testing techniques and perform this practice of fitting each time the respirator is worn.

IV. Cleaning and Disinfecting

Respirators should be cleaned and disinfected on a daily basis if used routinely throughout the day or less frequently if used less often.

Respirator cleanliness is particularly important in dusty environments or where respirators are shared by several individuals.

V. Storage

Respirators should be stored in a dry, clean storage area which is protected from extremes in temperature, sunlight, or physical damage.

VI. Inspection and Maintenance

Inspection schedules vary in frequency for specific types of respiratory protection equipment but should at least be inspected for damage or malfunctions both before and after each daily use. Records must be kept for emergency use respirators of at least monthly inspection dates and the inspectors findings. Developing a check list of items to look for is a good idea when inspecting any reusable respirator.

VII. Work Area Surveillance

Surveillance by the employer of the work area is required and includes identification of the contaminant, nature of the hazard, concentration at the breathing zone, and if appropriate, biological monitoring.

VIII. Inspection and Evaluation of Program

The effectiveness of the instituted program measures should be periodically evaluated. It is the employer's responsibility to administer the respiratory protection program so that it is effective. This includes mandatory employee participation where appropriate and provision of all other items cited herein.

IX. Medical Examination

It is required that a medical assessment of the employees ability to wear a respirator be performed prior to providing him with a respirator.

X. Approved Respirators

Only respiratory protection devices approved by NIOSH or MSHA, or both, can be used. Interchanging parts of different respirators nullifies approval.

Further information on respirators and instructions for establishing an appropriate respiratory protection program can be found in the NIOSH guide to Industrial Respiratory Protection, DHHS (NIOSH) Publication No. 87-116. Single copies are available free and can be obtained from:

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