114-14b

DETAILED INDUSTRIAL HYGIENE SURVEY

Formaldehyde Production
Reichhold Chemicals, Inc.
Hampton, South Carolina 29924

Participants

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GLOSSARY OF TERMS

adjusted volume	the volume of the sample corrected to standard temperature and pressure
Area sample	an air sample taken from a fixed location to estimate a contaminant concentration generally found within a limited locale
BDL	below the detectable limit
breakthrough	the possible overloading of a sample with contaminant, resulting in the possibility of sample loss reported when contaminant mass in the back section of a sample tube is greater than 25% of that found in the front section
BZH	breathing zone height, a height of approximately 5-7 feet above the ground
catch basin	a receptable designed to catch excess sample when withdrawing a process sample to reduce the potential of liquid contaminant from contaminating a process sample area
CIH	certified industrial hygienist
consecutive sampling periods	the combination of two or more successive lengths of sampling time resulting from two or more respective air samples
controlled exposure	a contaminant exposure that is regulated by engineering or work practices. Normally indicates an exposure below accepted OSHA standards.
CTA	control technology assessment, an evaluation of the methods used to reduce or prevent exposure to contaminants
dike	an embankment or wall to control potential liquid spills
double mechanical seal	a multiple seal arrangement that uses two single mechanical seals oriented back-to-back with a fluid filled space between them

GLOSSARY OF TERMS (continued)

engineering controls	the physical modification of a process or equipment used to reduce or prevent the release of contaminants into the plant area
EPA	Environmental Protection Agency
exposure	respiratory, eye, or skin contact with contaminant
face velocity	the time rate of change of position of air at the front open face of a hood
formalin	formaldehyde solution
fpm	feet per minute
GC	gas chromatograph
gpm	gallons per minute
GTI	Geomet Technologies, Inc., Rockville, MD
HCHO	chemical formula for formaldehyde
IH	industrial hygiene
L	liter
long-term exposure	contract with a concentration of contaminant during a long-term task
long-term sample	collection of contamiant occurring during a long-term task
long-term task	an operation of worker activity that require an extended period of time to complete, usually a full work shift
MeOH	symbol used for methanol
min	minute
mL	milliliter
MO	methanol oxidation
MRC	Monsanto Research Corporation, Dayton, OH
NA	not analyzed due to uncontrolled circumstances
ND	not detected; no indication of compound found during analysis
NIOSH	National Institute for Occupational Safety and Health

nonexcessive exposure	contact with contaminant that does not exceed the OSHA regulation
OSHA	Occupational Safety and Health Act
OSHA HCHO STEL	the amount of formaldehyde allowable in a sample of approximately 15 minutes, which is 5 ppm
OSHA HCHO TWA	the time-weighted average amount of formaldehyde allowable in a sample of approximately 8 hours - limit is 3 ppm
OSHA MeOH TWA	the time-weighted average amount of methanol allowable in a sample of approximately 8 hours - limit is 200 ppm
packed seal	an engineering control used to control emissions from nonstationary equipment parts. Normally consists of material within a packing gland that seals potential leaks when compressed
PEL	permissible exposure limit, the time-weighted average concentration to which nearly all workers may be repeatedly exposed, day after day, without adverse effect
personal sample	the collection of a volume of potentially contaminated air from the breathing zone area of a worker
PIHS	preliminary industrial hygiene survey; an in-plant survey conducted in order to gain approximate information in worker exposure, work practices, engineering controls, process flow, and the plant safety and health program
ppe	personal protective equipment; equipment worn by a working aide, as a respirator used to prevent potential worker overexposure to a contaminant
ppm	parts per million
short-term exposure	contact with a concentration of contaminant during a short-term task
short-term sample	collection of contaminant during a short-term task

GLOSSARY OF TERMS (continued)

short-term task	an operation or specific worker activity, the duration of which is part of a full work shift. The duration of the task normally ranges from 10 minutes to 2 hours.
single mechanical seal	the use of two sealing surfaces perpendicular to a shaft, one stationary, one rotating, to prevent leaks
source sample	an air sample taken at a fixed location within an artificially isolated area of an engineering control device. Used to estimate the expected release rate from that device.
standard conditions	temperature and pressure conditions to which the volume of all samples is adjusted so as to allow sample concentration comparison. Conditions used were 20°C (68°F) and 760 mmHg (29.92 in. Hg)
STEL	short term exposure limit; a concentration limit set for contaminant exposure usually over a 15 minute period
TWA	time-weighted average; the average concentration of a sample or a set of connective samples, weighted by the time sampled
walk through survey	a preliminary industrial hygiene survey

1. INTRODUCTION

The following detailed industrial hygiene/control technology survey report describes a four-day survey conducted at the Reichhold Chemicals, Inc., formaldehyde production plant, located in Hampton, South Carolina. This plant uses a metal silver catalyst to convert methanol to formaldehyde at a rated capacity of 50 million pounds per year. The plant was selected for a detailed industrial hygiene survey based on its abilty to control worker exposure to formaldehyde through worker practices and engineering controls.

1.1 PLANT PERSONNEL CONTACTED

The survey was conducted by Glen J. Barrett (GEOMET Technologies, Inc.) CIH, and David W. Dunn and Dennis J. Gault (Monsanto Research Corporation), on August 24-27, 1982. Mr. Frank Miley, plant manager, acted as the key contact person during the survey. One operator and two maintenance personnel under Mr. Miley's supervision were sampled for formaldehyde and methanol exposure during the survey.

1 2 SUMMARY OF ACTIVITY

The survey team met briefly with Mr. Miley on arrival at the plant on August 24, then set up a base of operations, and placed a pair of personal sampling pumps on the operator. A short walk-through reacquainted the survey team with the plant.

Industrial hygiene (IH) sampling began immediately on arrival Tuesday, August 24, and continued through the day shift on Friday, August 27. No sampling was conducted during second or third shifts due to the extremely limited plant staff. Similarity of operational duties to first shift and the plant manager's request for first shift sampling only (while he was present) made other shift sampling unfeasible. Table 1 shows the total number and types of sampling conducted during the survey. Personal exposure samples for formaldehyde and methanol were taken for the three individuals mentioned earlier.

TABLE 1. SAMPLES COLLECTED DURING IH SURVEY AT REICHHOLD CHEMICALS, INC., HAMPTON, SOUTH CAROLINA, ON AUGUST 24-27, 1982

	Formaldehyde		Methanol
Type	Long term	Short term	Long term
Personal	20	8	16
Area	25	5	25
Source	13	-	3
TOTAL[a]	58	13	44

[a] Total does not include 16 formaldehyde spiked samples and blanks and 6 methanol spiked samples and blanks.

Long-term (over two hours) personal samples were taken to evaluate the general worker exposure. Short-term (less than two hours) samples were taken to evaluate specific operations the worker conducted on a regular basis. Area samples were taken to determine the potential exposure of a worker in a specified area and to generally evaluate formaldehyde and methanol concentrations in the production and storage areas. Source samples were taken to evaluate the contribution of specific equipment to the overall area concentration and to evaluate the control achieved by this equipment.

Observations of operator procedures were also made during the survey. Control and process equipment were noted and discussed with Mr. Miley to aid in evaluating this equipment and comparing it to equipment at other plants.

A closing conference was held with Mr. Miley to discuss the future use of the data collected and to thank the plant for its cooperation

2. BACKGROUND

The National Institute for Occupational Safety and Health (NIOSH) and the U S. Environmental Protection Agency (EPA) have entered into an Interagency Agreement to perform a study that will determine the levels of pollutants to which workers in the formaldehyde production industry are exposed and that will evaluate the effectiveness of control technologies currently used to minimize exposures

EPA contracted with Monsanto Research Corporation (MRC) to perform the study on the formaldehyde production industry, under EPA Contract No. 68-03-3025, entitled "Technical and Engineering Services " MRC was assisted in the study by personnel from GEOMET Technologies, Inc., (GTI).

2 1 OBJECTIVES OF THE INDUSTRIAL HYGIENE/CONTROL TECHNOLOGY ASSESSMENT (IH/CTA) STUDY

The objectives of the IH/CTA study are to:

- evaluate the state-of-the-art control technology in the formaldehyde production industry,
- evaluate the effectiveness of industrial hygiene control programs to control these potential hazards,
- identify potential hazards to workers,
- evaluate these potential hazards for the effects on workers,

- assess current formaldehyde production technology with respect to control of potential exposures of workers,

- assist the transfer of control technology inter- and intra-industry, and

- identify processes for which engineering controls are not available or are ineffective, where further research and development are needed, and to indicate priorities for application of control technology.

The study is divided into two phases, preliminary surveys and detailed surveys.

As part of this project, preliminary industrial hygiene surveys (PIHS) were conducted at 11 plants, representing a cross-section of formaldehyde production facilities. Control equipment and worker practices were discussed and observed and walk-through surveys were conducted at each plant. Potential exposures to hazardous agents and technologies used to control those agents were identified. Reports were prepared on the findings from these surveys.

The following sections briefly describe the objectives of this project.

Four plants were selected from the eleven for detailed industrial hygiene surveys based on the preliminary survey findings. The detailed industrial hygiene surveys included the following activities:

- observation of operator work practices,

- quantitative personal sampling,

- evaluation of engineering control techniques, monitoring devices, and personal protective equipment used by the industry to reduce exposures, and

- preparation of a detailed plant visit report for each of the four surveys, detailing worker practices and evaluating the engineering controls used by the plant; this report is one of these four reports.

3. DESCRIPTION OF THE PLANT

The Reichhold Chemicals, Inc., (RCI) Hampton, South Carolina, plant is located in a rural area outside of Hampton, South Carolina. Constructed in 1958 to supply a nearby consumer, the plant produces 50% formaldehyde solution which is blended with water or methanol to meet customer specifications. Formaldehyde is the only product of the plant. Sixty percent of the product is piped directly to an adjacent consumer, with the remainder loaded into tank trucks and rail cars for customer delivery in nearby areas.

The plant area, shown schematically in Figure 1, includes a process area, methanol unloading and storage area, formaldehyde storage and loading areas, and an office building. The process area, shown in Figure 2, has a semi-enclosed and roofed reactor area (left) adjacent to other process operations that are not enclosed (center). Methanol, received in rail tank cars, is stored in a large isolated tank and supplied to the process via an underground pipe. Formaldehyde storage and blending facilities are on the opposite end of the plant from the methanol storage, across a plant road from the process area. Shipments to consumers are loaded into tank trucks adjacent to this formaldehyde storage area, and rail cars are loaded adjacent to the methanol unloading and storage areas.

The office building adjacent to the process (on right in Figure 2) houses the management offices and the process control room which doubles as a process sample analytical laboratory. Workers spend a majority of their time in this area.

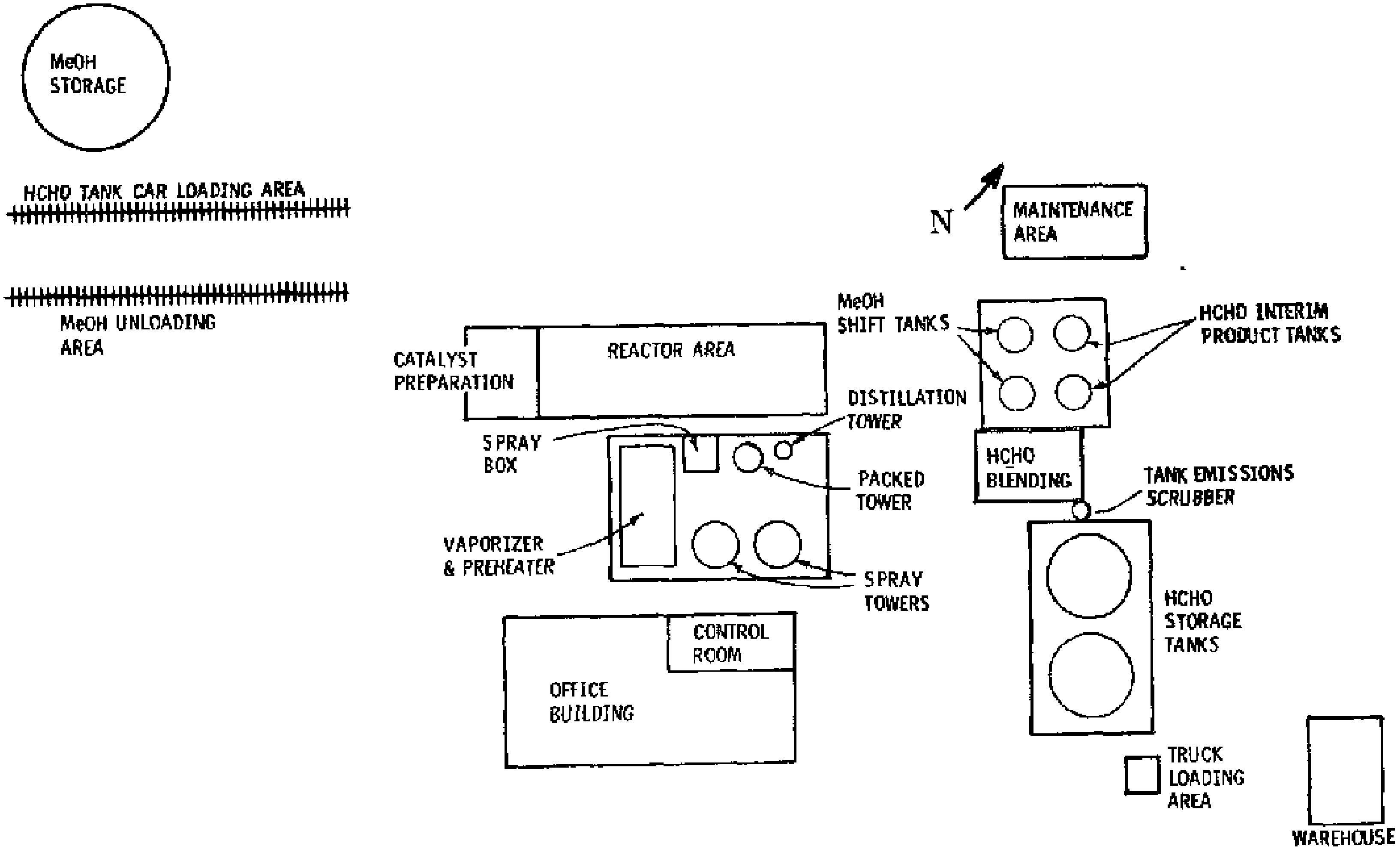

Figure 1. Schematic of the plant area.

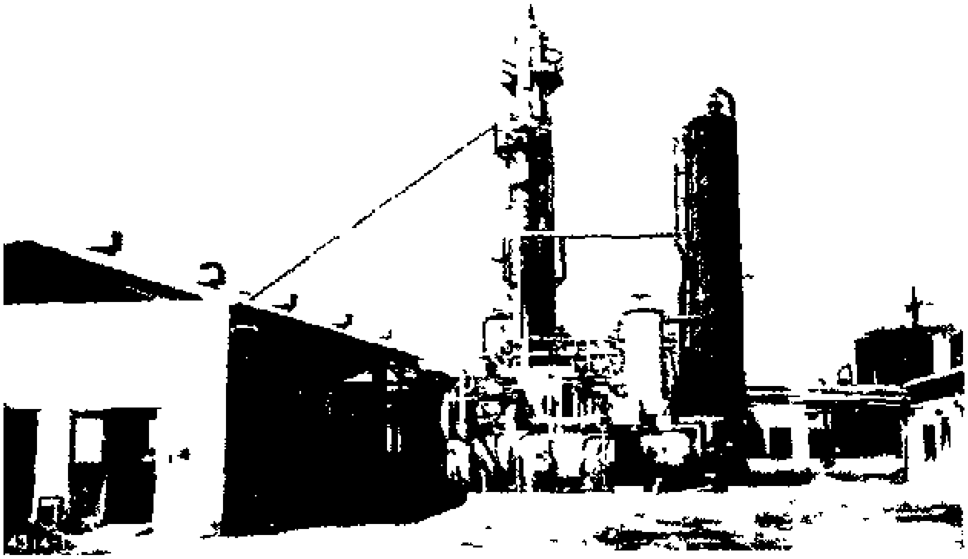

Figure 2. Production process area.

The plant, which normally operates on a 7 day per week, 24-hour per day schedule using four shifts, currently has eight employees. Depressed economic conditions have reduced this normal operation schedule to 5 days per week and three shifts. The work force is broken down into three categories: two supervisory personnel, two maintenance workers, and four operators. The supervisory and maintenance personnel are assigned to the day shift, but are on 24-hour call for major plant breakdowns or emergencies. Operators are assigned one per shift and have the following duties: monitor and control the process, sample the process and analyze the samples, blend the 50% formaldehyde solution to meet customer specifications, unload methanol and load formaldehyde, and assist maintenance when necessary. Maintenance workers are responsible for process maintenance - including catalyst preparation, daily process area hosedowns, groundskeeping, and general maintenance of the plant.

4. PROCESS DESCRIPTION

Formaldehyde is produced by a silver catalyst process. This process is based on the dehydrogenation-oxidation reaction of methanol as it passes through a silver catalyst bed. Conversion efficiency of the process can range from 65% to 90%, depending on the age and retention time of the catalyst bed. Methanol recovery and concentration of the formaldehyde solution is normally necessary to yield a usable product.

The general process used at this plant is schematically shown in Figure 3 Methanol, delivered by rail tank car and stored in a large bulk storage tank, is mixed with filtered air and vaporized The methanol-air mixture is fed through manifolds to individual tubular reactors containing the silver catalyst and is converted to formaldehyde. The hot gases are quenched with a weak formaldehyde solution, in a spray box, producing a 40% formaldehyde, 20% methanol solution This solution is cooled in a heat exchanger and stored in interim storage tanks.

The scrubbed gas from the spray box passes through two spray towers and a packed tower It flows countercurrent to laboratory wastewater and fresh water introduce in the packed tower. The water flows from the packed tower back through the spray towers and becomes the weak formaldehyde solution which is fed to the spray box. The residual gas from the packed tower is then released to the atmosphere. This exhaust gas contains approximately 73% nitrogen and 20% hydrogen, but little or no formaldehyde.

The 40% formaldehyde solution from the spray box is stored in a set of interim product tanks and is concentrated to 50% formaldehyde

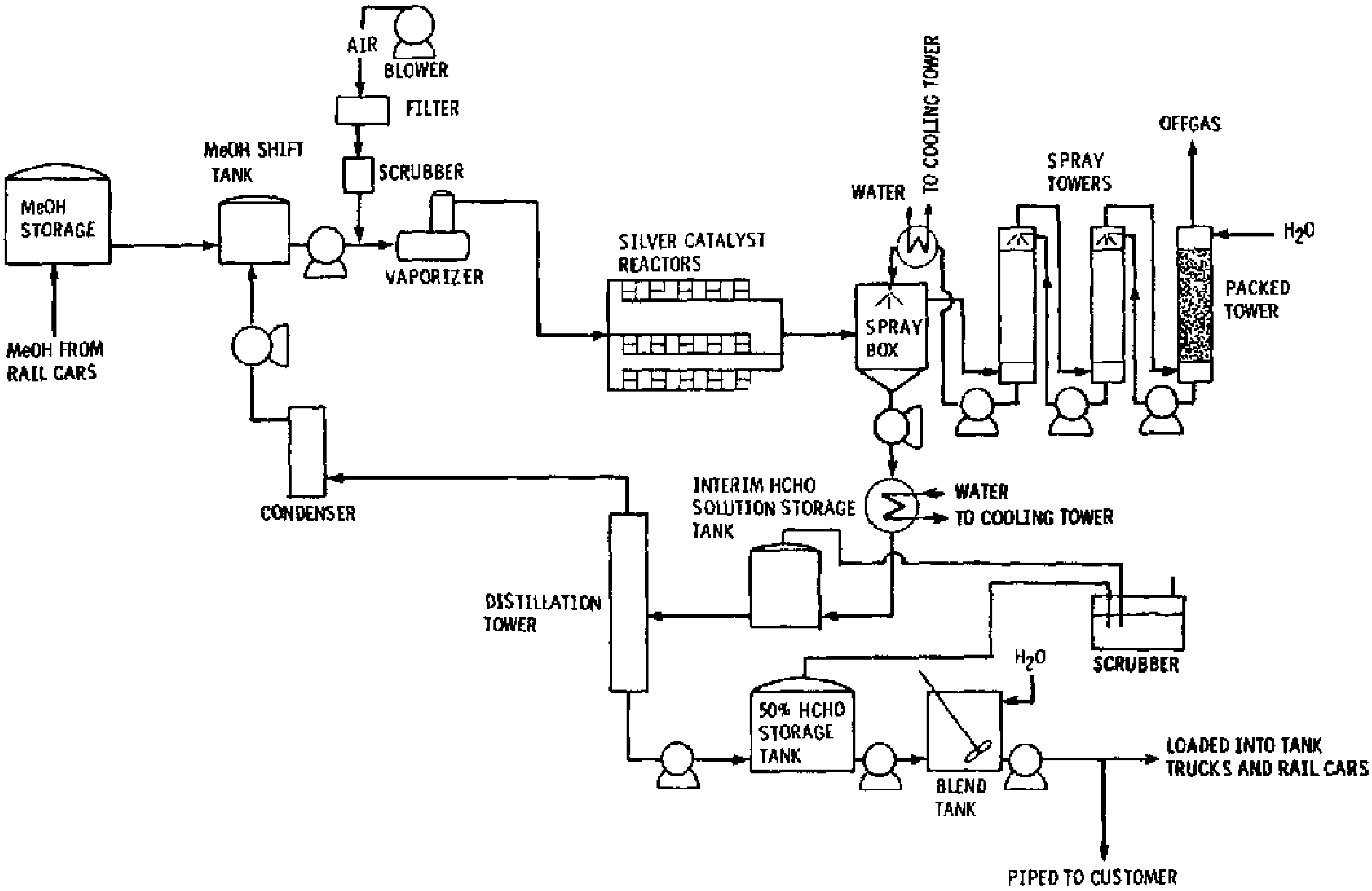

Figure 3. Schematic of Hampton formaldehyde process.

in a distillation column. A scrubber is located on this tank to condense and hence control formaldehyde emissions from it. Methanol removed to concentrate this solution is recovered and recycled to the methanol shift tank, and product (50%) formaldehyde solution is sent to steam-heated storage tanks. Formaldehyde shipments are prepared in a blending tank where the formaldehyde content is adjusted to meet the customer specifications. The product is then piped directly to an adjacent plant or loaded onto tank trucks or rail cars for delivery.

5. DESCRIPTION OF PROGRAMS

5.1 INDUSTRIAL HYGIENE AND SAFETY

The Corporate Office provides interpretations and guidelines to the plant on governmental rules, regulations and corporate policies. It periodically audits the plant program, and may become more involved if unusual circumstances occur. The plant is responsible to the RCI Regional Manager for its safety policies and implements its safety program with considerable independence from the Corporate Office.

Corporate health and safety resources are available to the plant upon request. Interaction with the corporate level has been at a minimum, however, due to the Hampton plant's freedom from problems, good record, and an active control program implemented by the plant manager. The plant conducts a monitoring program of the control room area to evaluate worker exposure to formaldehyde.

Contingency procedures for fire, explosion, and tank rupture emergencies are well-defined. Fire department personnel have visited the plant and been provided with a copy of the contingency plan, and a full description of the processes involved. Spills are controlled by diking around the methanol unloading areas and all of the storage tank areas. In addition, minor amounts of unrecyclable waste materials, spill materials, flushing material from the laboratory, and runoff can be diverted to a pair of holding basins at the rear of the site.

The last lost-time accident at the Hampton plant was in 1974. A worker incurred a chemical splash in the eye during a drum filling operation, which resulted in the loss of one work day. In 1977, a glass chip in the eye from a beaker containing caustic soda resulted in first aid treatment, but no lost time or followup treatment was required.

5.2 OCCUPATIONAL SAFETY AND HEALTH TRAINING

All employees have had first aid courses and have taken a course given by the State of South Carolina on hazardous chemicals. Safety meetings are held monthly during which environmental issues are also discussed. Since the newest employee has been at the plant for 12 years, training of new employees has not been considered.

5.3 PERSONAL PROTECTIVE EQUIPMENT (PPE) AND SAFETY EQUIPMENT

An extensive set of PPE is issued or made available to the employees. This is detailed in the plant safety rules which are listed in Appendix A.

Emergency eye wash and shower units are located at the formaldehyde truck loading area, next to the refrigeration unit in the production unit, and at the methanol unloading/formaldehyde rail car loading area.

The following PPE is required for specific operations listed:

Formaldehyde Loading

Water-proofed cotton gloves

Methanol Unloading

Neoprene gloves

Formaldehyde Solution Sample Withdrawal

Neoprene gloves

Formaldehyde Storage Tank Entry

Air-supplied respirator
Water-proofed cotton gloves

Maintenance-Formaldehyde or Methanol Leak Repair

Full-face gas mask approved for acid gases, organic vapors, dusts, and mists for a major leak

Water-proofed cotton gloves if there is a potential for formaldehyde skin contact

A continuing effort to eliminate situations requiring the routine use of PPE has been successful (see Section 7) e.g., tank entries are minimized by mounting tank heating coils on most tank entry covers, local exhaust ventilation control is being used during formaldehyde truck loading operations.

5.4 MEDICAL PROGRAM

All employees were given a pre-employment physical examination Annual physicals are required, and include specific attention to the respiratory tract.

Medical services, in case of on-site injury, are available from physicians and the hospital in Hampton, less than 2 miles from the plant.

6. WORK PRACTICES

6.1 GENERAL PROCEDURES

6.1.1 Operators

Operators are assigned one per shift and have the following duties: monitor and control the process, sample the process and analyze the sample, blend the 50% formaldehyde product solution to meet customer specifications, unload methanol, load formaldehyde, and assist maintenance when necessary.

Operators spend approximately 70-80% of their time in the control/lab room monitoring the process and analyzing samples. Each shift is a total of eight hours, with the operator taking a 15-minute lunch break in the control/lab room.

The plant is currently being shut down at noon every Friday due to economic and marketing conditions. For the remainder of the Friday day shift, the operator flushs down the distillation column and the process heat exchangers with air, followed by water. He also checks all process valves for leaks. No operators come on shift after the first shift on Friday through the weekend. Preparations for restarting the unit begin on the first shift the following Monday.

6.1.2 Maintenance

Maintenance workers are responsible for process maintenance including catalyst preparation, catalyst changeover in the converters, groundskeeping, and general maintenance of the plant. If a converter leak is smelled, the maintenance worker is responsible for finding the leak using a hand-held propane torch and repairing or shutting off the leak. They are assigned to the day shift on Monday through Friday, but are on call for major plant breakdowns or emergencies. Lunches are eaten on-the-job, during the 8-hour shift.

6.2 METHANOL UNLOADING

Methanol is received and unloaded from rail cars, with approximately three rail cars unloaded weekly. Three rail cars can be unloaded simultaneously.

Prior to unloading a car, the operator withdraws a methanol sample for analysis from the car through the top hatch. This procedure will be described in more detail in Section 6.3 After sample withdrawal and analysis, he attaches a quick-connect flexible line to the rail car for bottom unloading.

It takes 8-10 hours to unload one rail car One operator starts unloading a car and the operator on the next shift completes the process Once unloading is initiated, the operator leaves the unloading area, unless an emergency occurs The next shift operator then bleeds and disconnects the unloading line after unloading is complete, and closes and secures the top hatch.

6.3 METHANOL SAMPLING AND ANALYSIS

A methanol sample is removed from each rail car by the operator prior to unloading. The operator obtains a sample by opening the top hatch and dipping an open glass bottle, held in his gloved hand, into the methanol (Figure 4). After a sample is obtained, it is capped and taken to the control/lab room. The boiling point is determined within the smaller of two laboratory hoods located within the control/lab room. The sample bottle is uncapped

Figure 4. Operator taking an MeOH sample from tank car. No dip extension--used rubber gloves.

and 100 mL of methanol is measured in a graduated cylinder inside the hood. The methanol is poured into a round-bottom flask within the hood, and the methanol is brought to a boil to determine its boiling point. All of these activities are done by a single operator.

6.4 FORMALDEHYDE LOADING

6.4 1 Truck Tank Loading

Approximately seven to eight tank trucks are loaded per week by the operator. The operator initially opens the hatch and inserts a dip tube and vacuum local exhaust duct from an elevated work platform into the tank.

The operator turns on the exhaust fan at the loading site, and then turns on the controls located in the blending shed to initiate loading. He leaves the area and returns occasionally to check filling progress.

Since loading is metered automatically, the operator only spends approximately 3 minutes of the total average loading time of 40 minutes per truck, at the loading site. Reduced exposure time at the loading site minimizes the worker's exposure to this source of formaldehyde gas.

Once loading is complete, the operator returns to the blending shed and operates controls to flush the feed line with air. The dip tube and exhaust duct are removed from the truck; a sample is manually taken by lowering an open glass jar into the solution, and the hatch is closed and secured. Any formaldehyde spills on the truck or ground are then hosed down with water to dilute the formaldehyde.

A single tank truck was loaded during the survey period.

6.4.2 Rail Car Loading

Approximately three rail cars are loaded per month by the operator. The rail cars are loaded with formaldehyde adjacent to the tracks where methanol is unloaded. He initially opens the top hatch and inserts the dip tube into the car. He then leaves the area to initiate loading through operation of controls within the blending shed. It takes approximately two hours to load a single rail car.

The operator is away from the area for the entire loading period. He returns to the blending shed once loading is complete to operate controls for flushing the loading line, first with air and then with water. As with truck loading, the loading is metered by weight and time, reducing the possibility of overfilling and the operator's exposure time in the loading area.

Once the line has been flushed with air and water, the operator returns to remove the dip tube from the car, manually obtains a sample by lowering an open glass jar into the solution, closes and secures the hatch, and hoses any spilled formaldehyde off of the car and ground.

A single rail car was loaded during the survey period.

6.5 FORMALDEHYDE SOLUTION SAMPLE WITHDRAWAL AND ANALYSIS

The operator usually withdraws two process samples from the absorber (spray box) and two samples from the distillation column (stripper) per shift. Each operator schedules sample withdrawal differently. As an example, one operator may take a single sample from either the absorber or distillation column every two hours. Another operator on another shift may take a sample from the absorber and one from the distillation column at one time during the first half of the shift, and then take the remaining absorber and distillation column samples at one time during the second half of the shift.

The operator withdraws a sample of either the absorber (Figure 5) or distillation column (Figure 6) from a short sample spigot fitted with a ball valve. He purges the line into a 250-mL Erlenmeyer flask and dumps the purge into a catch basin near the sample point (Figure 7). The formaldehyde solution is directed from the basin by piping to the makeup water unit for the absorber or spray tower. Once the sample line is purged, the flask is filled and stoppered (Figure 8). The stoppered flask is carried to the control/lab room where the percent methanol, formic acid, and formaldehyde are determined. All analyses are performed in the larger of the two local exhaust ventilation laboratory hoods (Figure 9). All of these activities are done by the operator.

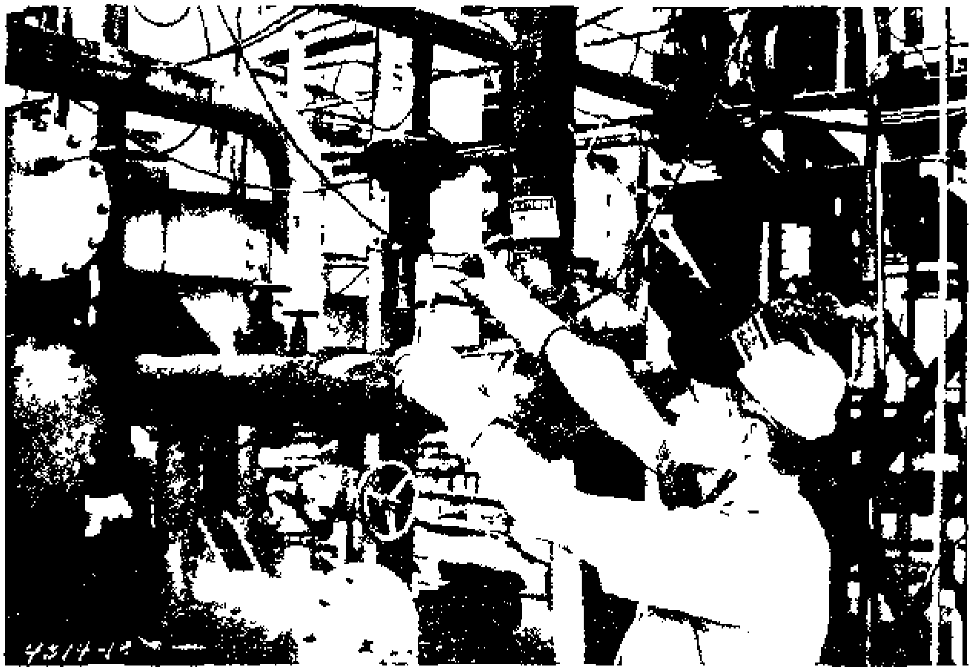

Figure 5 Process sampling at absorber/heat exchanger by operator. Note gloves and no respirator. Note formaldehyde tubes at operator's ear

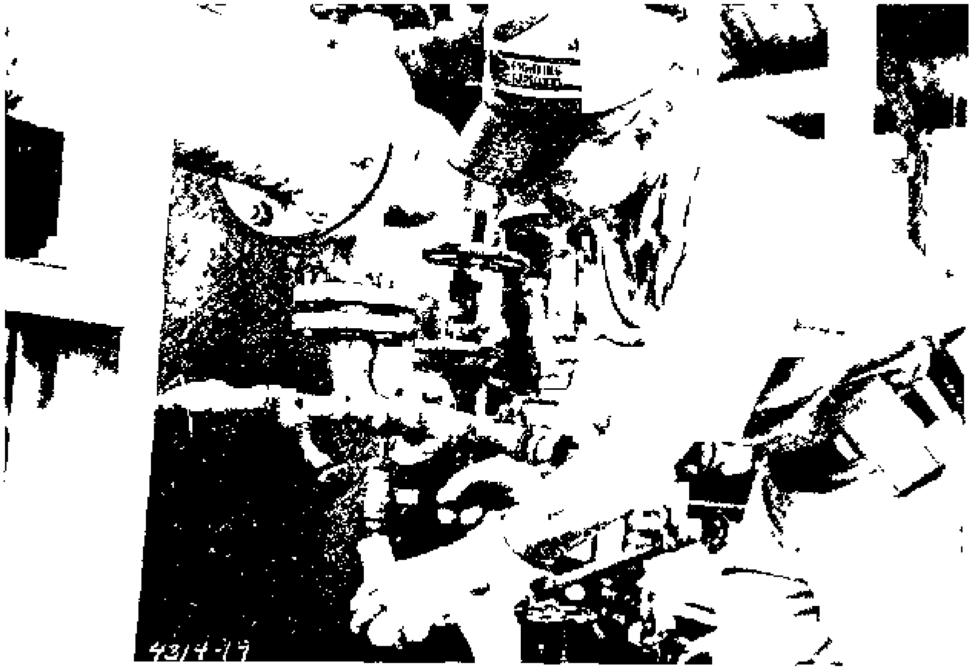

Figure 6. Sample tubes on operator's shoulders.

Figure 7 Operater discarding process sample line purge into makeup water system Note gloves.

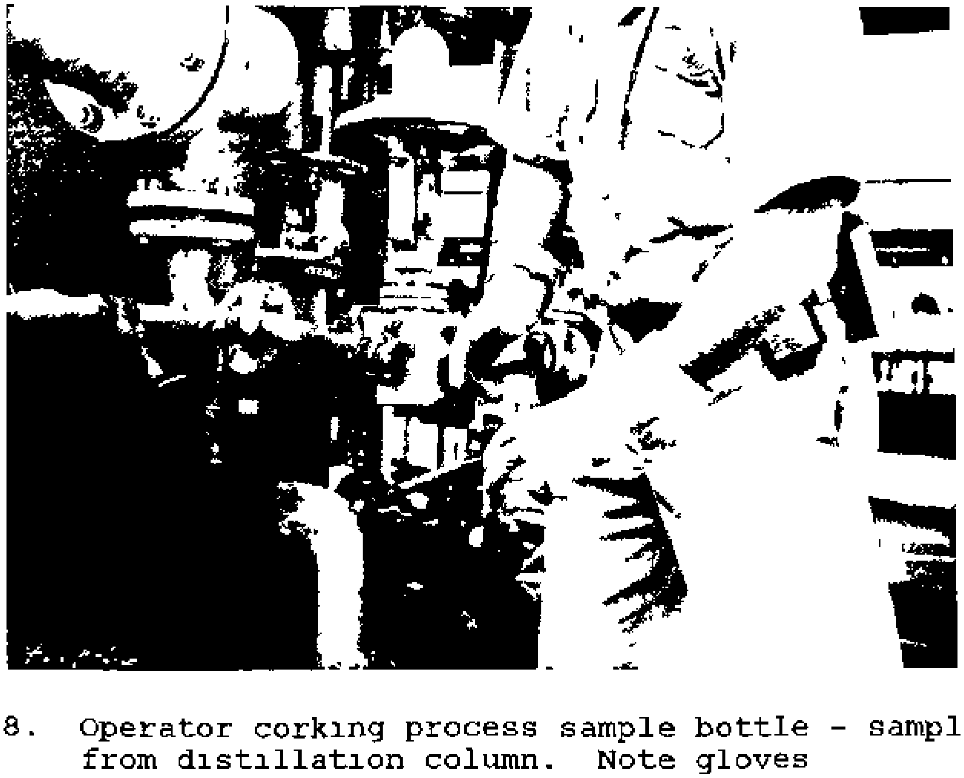

Figure 8. Operator corking process sample bottle - sample from distillation column. Note gloves

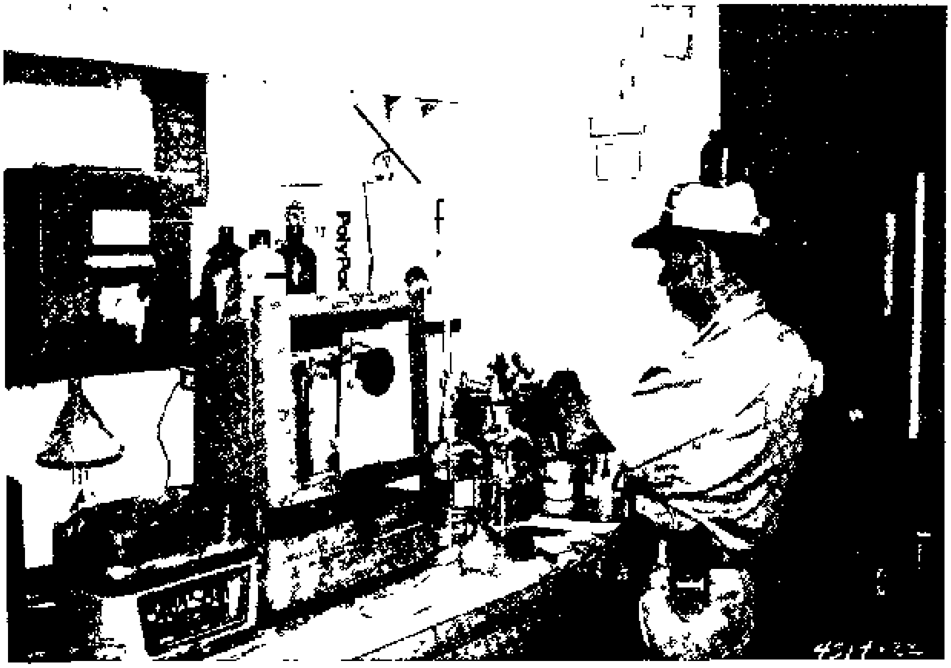

Figure 9. Operator conducting process sample analysis. Note gloves and sign above operators head. Also note personal sample pumps and HCHO tube on shoulder.

The percent methanol is determined by running a specific gravity test on a portion of the sample; percent formic acid is determined by titrating a portion of the sample with sodium hydroxide; percent formaldehyde is determined by titrating a portion of the sample with sulfuric acid Once the analyses are complete, the unused portion of the sample and all waste is dumped in a sink located within the laboratory hood. The waste is conducted to the makeup water unit for the absorber or spray tower.

The operator withdraws a single sample from each tank truck or rail car which has been loaded with formaldehyde. This is accomplished by manually lowering an open-glass jar in a holder at the bottom of a chain into the tank. The jar is filled, pulled out, and immediately covered with a screw-on cap. The sample is transported to the control/lab room where its specific gravity, percent formaldehyde, and percent formic acid are measured. These analyses are performed as described previously in this section within the larger of the two laboratory hoods. All waste is dumped into the sink within the laboratory hood. All of these activities are done by the operator.

Occasionally, an operator will take a sample from a line off of the blend tank prior to loading a tank truck or rail car. This sample would be taken instead of a sample taken directly from the tank truck or rail car The sample is taken from a sample spigot into a glass jar. After filling, the jar is covered with a screw-on cap and transported to the control/lab room. Here, a specific gravity test and determination of percent formaldehyde and formic acid analyses are run within the larger of the two local exhaust ventilated laboratory hoods. Waste is dumped down the sink within the lab hood. Again, all of these activities were performed by the operator.

7. CONTROL STRATEGY

Several areas of the formaldehyde operation that present exposure potential are discussed below with respect to the control technology applied. Exposure control is primarily achieved by using a process that is completely enclosed - except for the methanol entry point, formaldehyde discharge point, and process sample points.

7.1 METHANOL UNLOADING AND STORAGE

Methanol received by the plant is unloaded from railroad tank cars by the process operator in the area shown in Figure 10, which is approximately 200 feet from the main production area.

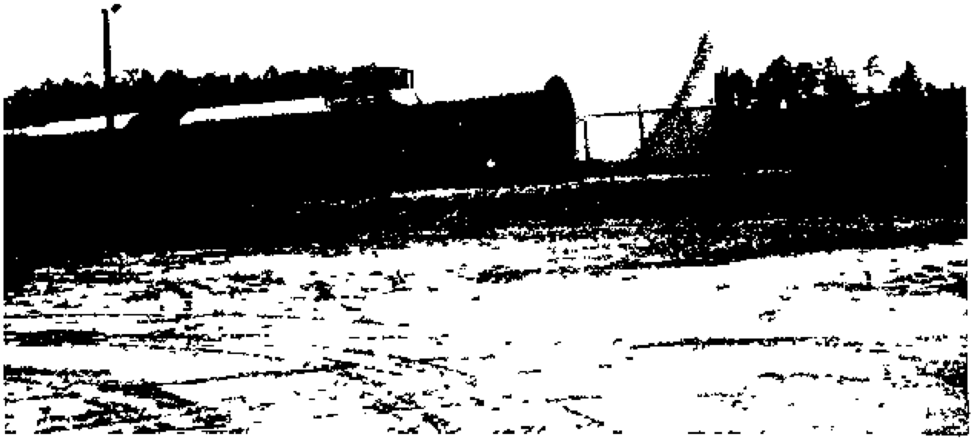

Figure 10. Methanol bulk storage and unloading

Prior to unloading, the operator chocks the wheels, grounds the tank car, and opens the bolted top lid of the tank car (Figure 11). A small sample is taken from the tank and is analyzed to ensure methanol purity The tank car lid is left partially open. This small gap (approximately 2 inches) does not present an exposure problem because a vacuum is created as the tank drains, which draws air into the tank and reduces the escape of methanol vapors. The operator removes the cap from the standard tank car discharge outlet (shown capped in Figure 12), and connects a quick-connect adapter to the outlet which allows a reinforced flexible quick-connect tube to be attached (Figure 13). The quick-connect fitting on the tube uses a neoprene gasket to reduce methanol leakage during unloading.

Figure 11. Operator opening top of methanol tank car for unloading.

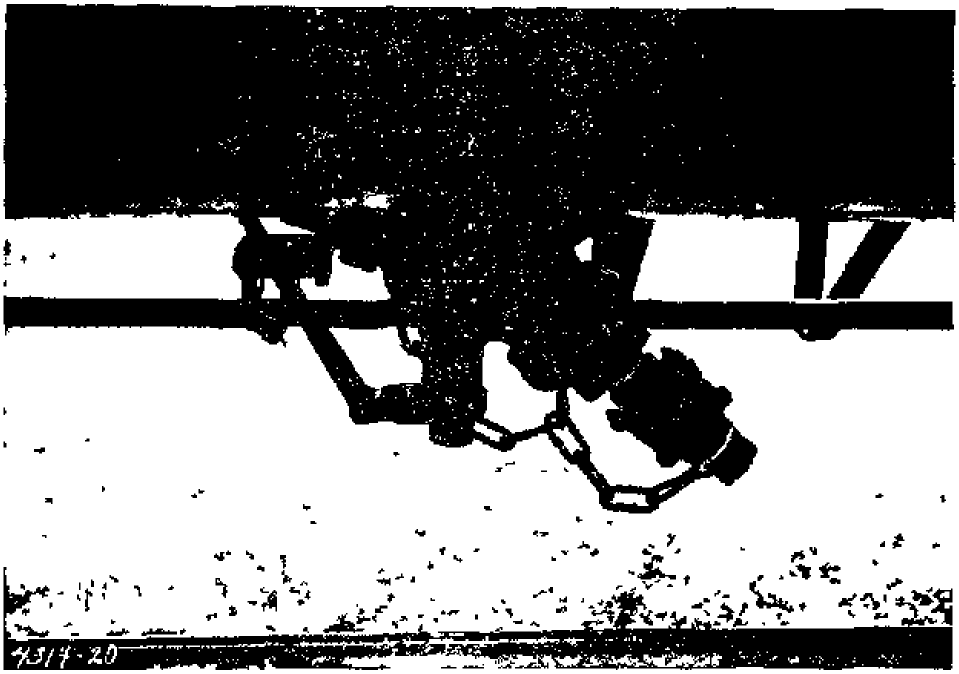

Figure 12. Bottom valve and closure setup for methanol tank cars. Note valve lever on left and cap on right.

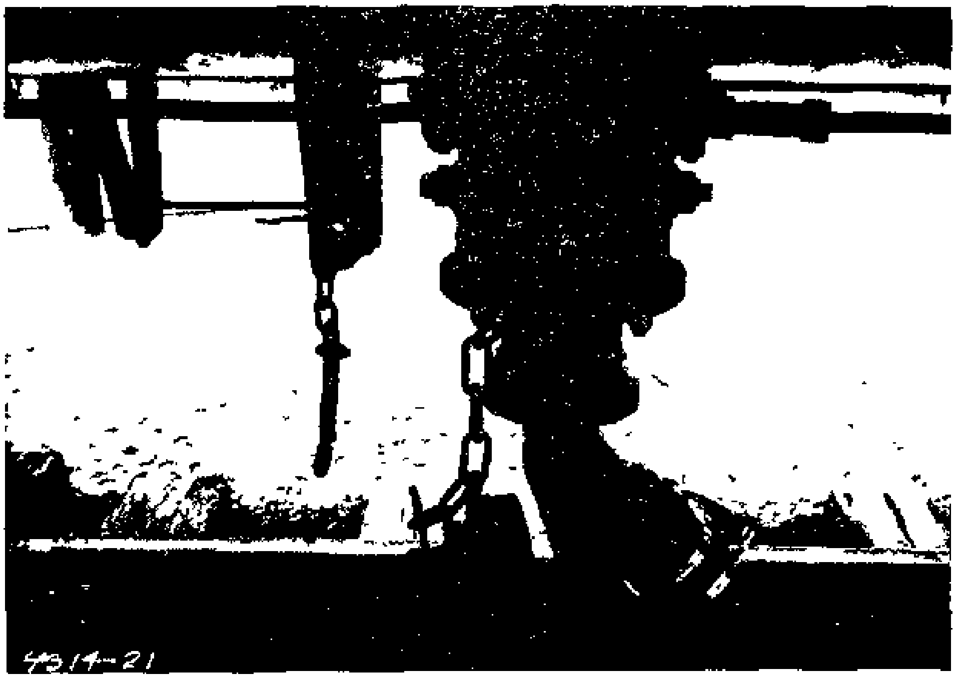

Figure 13. Methanol unloading setup on bottom valve Note adapter and quick-connect. Valve lever is in front.

Methanol is pumped from the tank car through the hose and piping to either the bulk methanol storage tank, located adjacent to the rail siding, or to the methanol shift tank. A Goulds centrifugal pump fitted with a John Crane single mechanical seal is used. No methanol is used for lubrication in the mechanical seal. Carbon rotary seals on ceramic stationary faces are used in the seal. All pumps are checked periodically, with leaking pumps repaired as soon as possible. No maintenance is done on seals that are not leaking, regardless of length of service. This pump is left primed at all times, but a glass jug of methanol, (Figure 14) is available for priming if needed. This open bottle, located beneath the tank car loading platform, is not covered or protected from breakage

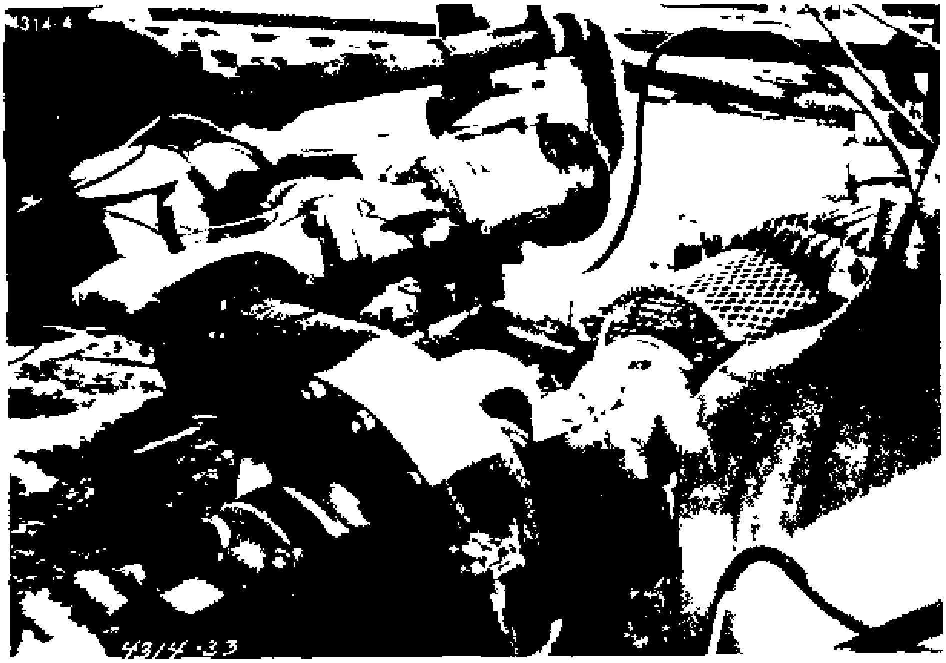

Figure 14 Methanol unloading pump and priming mechanism.

No caps are placed on the flexible hoses when not in use, nor are the hoses regularly disconnected from the unloading pump. Accidental spills in the unloading area are collected by surface drainage in a nearby sump, approximately 100 feet from the unloading dock, and then pumped to an equalization pond before treatment at a local wastewater public treatment works. An emergency shower and a small fire extinguisher are located next to the methanol unloading area.

7 2 METHANOL STORAGE AREA

Methanol is stored in a one-million-gallon storage tank (Figure 10) behind the unloading area and in two smaller shift tanks near the production unit Methanol is delivered from the large tank via an underground pipe The large tank is diked, grounded, has an external level indicator, and is equipped with a flame arrester on the breathing pipe. The smaller methanol shift storage tanks, also diked, grounded, and equipped with flame arresters, have an automatic level switch which maintains the level in the tank by drawing methanol from the large tank as needed. An overfill pressure switch is also in place to shut off the transfer pumps when the tank reaches a certain fill level, preventing accidental spills and reducing potential worker exposure.

7.3 CONVERTER AREA

The Hampton plant uses several banks of small (~6-inch) tubular reactors packed with metal silver catalyst to convert methanol to formaldehyde. Figure 15 shows these small reactors. Flexible metal tubes are used to feed methanol from methanol manifolds to the converters, which are connected directly to the product formaldehyde manifolds Each individual converter has separate valving that can isolate the converter, allowing leaking reactors to be locked out of the system. Flanges and high temperature gaskets also protect the system against leaks The converters

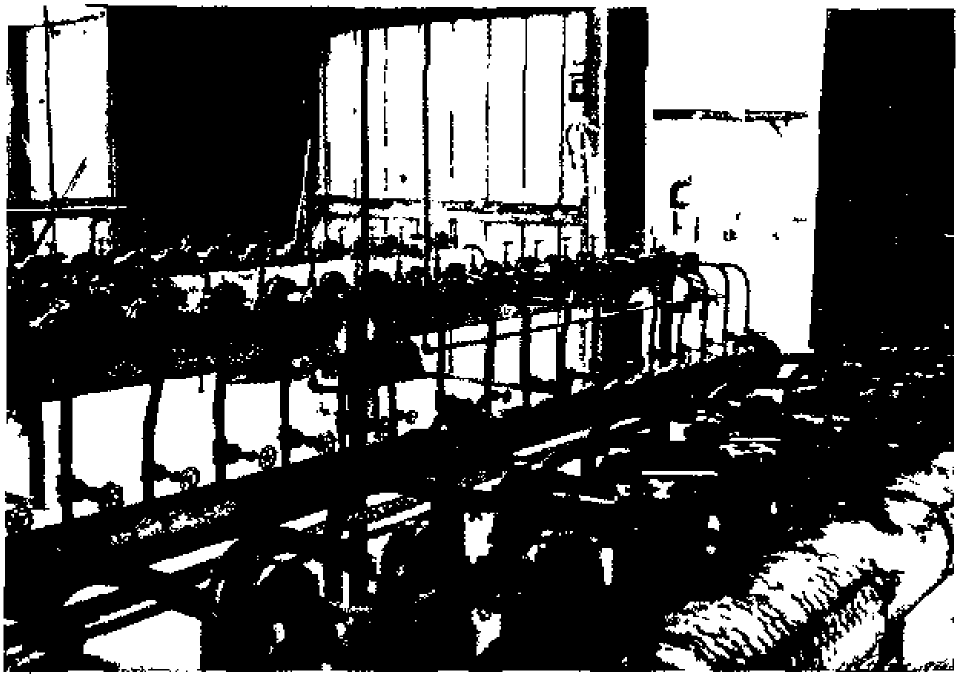

Figure 15. Reactor area.

are checked daily by smell for obvious leaks and during start up using a hand-held propane torch. The use of a propane torch is not considered to be a safety hazard since the formaldehyde concentrations being checked are far below the flammability limit.

The converters are housed in a semi-open building, as shown in Figures 2 and 16. This building was completely enclosed at one time, but had the sides removed to reduce heat and fume hazards to the workers. The semi-open construction allows air cooling of the reactors. However, temperatures in the converter structure are still above 100°F.

The vaporizer, which combines filtered air and preheated methanol into a hot gas mix, is located adjacent to the structure. The blower used to push the air into the process is noisy, having a noise level which has been measured at ~85 dbA. Methanol is pumped from the methanol shift storage tanks through a heat exchanger to

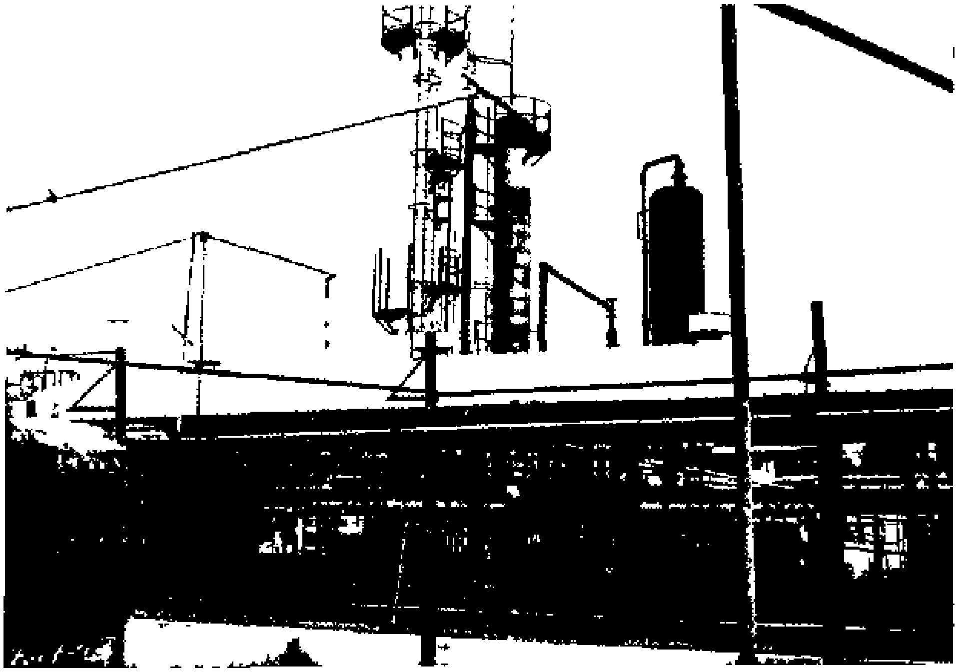

Figure 16 Converter area building (note no sides). In background left to right, blending building, distillation column, packed tower, tall spray tower.

the vaporizer using a leakproof centrifugal pump, one in which all moving parts are enclosed within a surrounding gland.

The nature of a closed process makes additional controls beyond the natural ventilation in this area unneeded. All valves were tightly packed to prevent leaks and appeared well maintained. This is supported by the weekly start-up and shut-downs the plant goes through in which no leaks are apparent The results of the area sampling done during this visit support the effective application of controls in this area.

7.4 ABSORPTION AND DISTILLATION

The absorber system as shown in Figure 3 consists of a spray box, two spray towers, and a packed tower that reduces formaldehyde concentrations in the final emissions to ppm levels. In addition, several heat exchangers are in use to recover heat from the hot gases coming from the converters. Figure 17 shows the two spray towers and packed column as well as the distillation column.

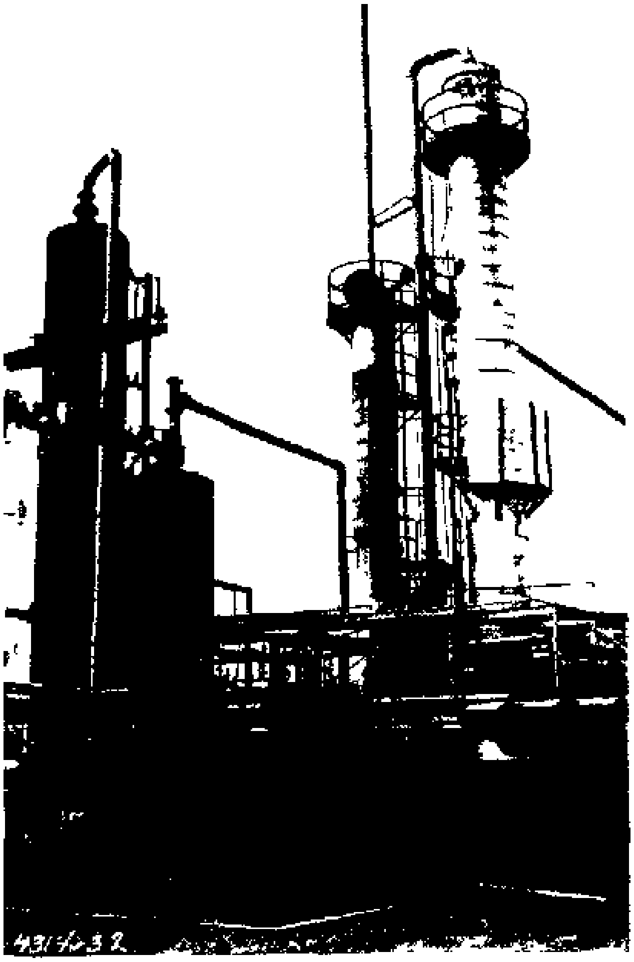

Figure 17. Production area, left to right - tall spray tower and short spray tower, packed tower with stack, distillation (stripper) column, air cooler and makeup water. Sample discard on right corner of cooler. Note diking.

Water and formaldehyde solutions for these operations are pumped using Gould centrifugal pumps with John Crane single mechanical seals. A majority of the six pumps in use recycle a portion of the solution back to the pump seals to lubricate and clean the seal faces. Plant experience with these pumps indicate that both seals (lubricated and nonlubricated) types are equally effective. All pumps were clean, with only minor spots of paraform in the pump housing.

At an earlier time, only the packed tower was used to absorb the hot formaldehyde gas. This led to high release rates of formaldehyde and prompted the company to install the additional spray towers Emissions from the packed tower now average about 5 ppm of formaldehyde. Further characterization of the emissions is as follows:

Component	Percent
N_2	75 16
CO_2	4.37
CO	0.16
CH_4	0 31
H_2	19.99
H_2O	saturated

The plant manager has been attempting to get permission to incinerate the gas to recover its heat value which, he estimates, would increase the profitability of the plant

The distillation column, which reduces the methanol content and concentrates the 40% formaldehyde solution, uses identical Gould pumps and John Crane seals No paraform was seen on the pump housing, nor in the distillation area. The 40% formaldehyde solution is pumped to the distillation column from two interior storage tanks in the diked area that also includes the methanol shift tanks. These interim storage tanks will be discussed in Section 7.6.

A safety shower and eyewash are within easy access by workers in these areas. The shower is adjacent to process sample points for the spray box and distillation column.

7.5 PROCESS SAMPLING

Process sampling is conducted every four hours from the product line of the distillaton column and from the discharge heat exchanger for the spray box shown in Figures 18 and 19, respectively.

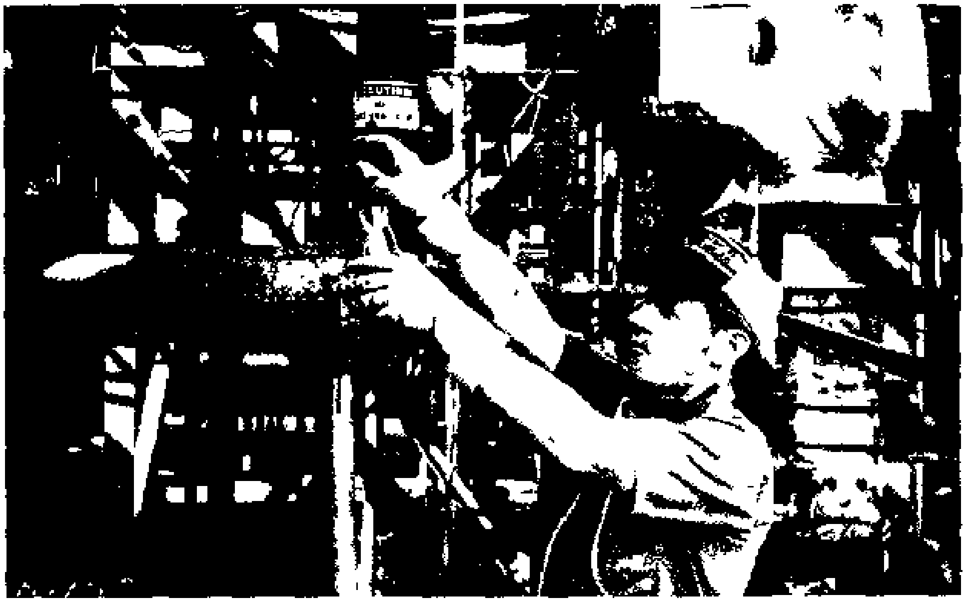

Figure 18 Operator sampling process at absorber heat exchanger. Note gloves, no respirator, height of port.

Figure 19. Operator taking process sample from final product line Note gloves and personal sample pumps.

Small ball valves are used as the sample ports on the main lines. Sampling lines are purged into an Erlenmeyer flask, with the purge dumped into a sample discard station. The sample is then taken in the same Erlenmeyer, the flask is capped and carried to the lab for analysis in a large, open hood shown in Figure 20. Each sample point has a bucket under the discharge to catch any spills. The discarded purge is recycled to the process as part of the makeup water used in the absorber system.

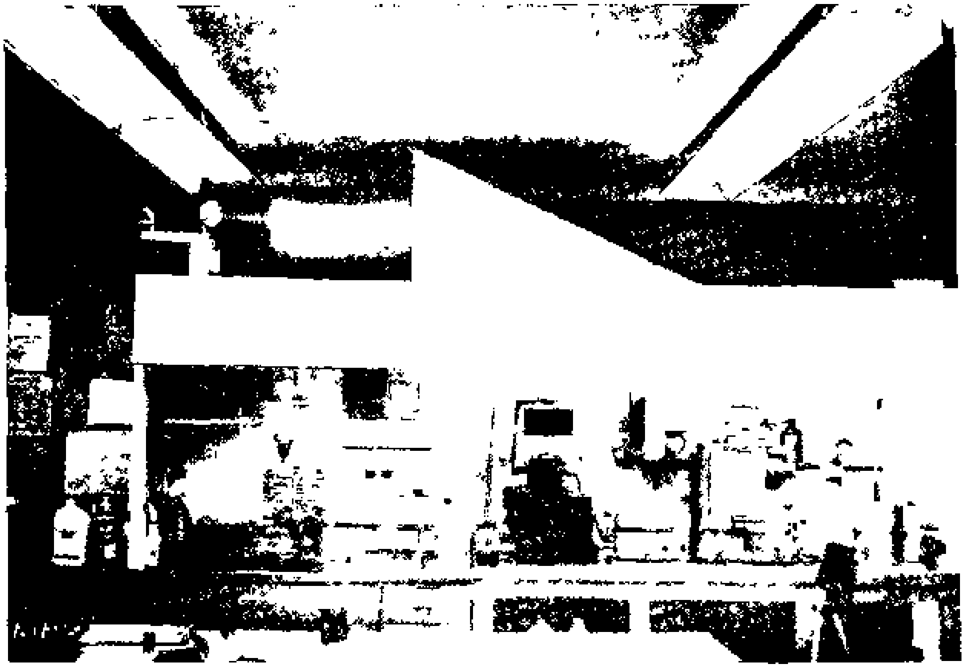

Figure 20. Control room hood (HCHO). Area sample on right; velometer in center on table, sample discard site on right.

7.6 FORMALDEHYDE STORAGE

Formaldehyde is stored in two areas of the plant; one area for interim storage prior to solution concentration in the distillation column (Figure 21), and the other (Figure 22) for final product storage (see Figure 1).

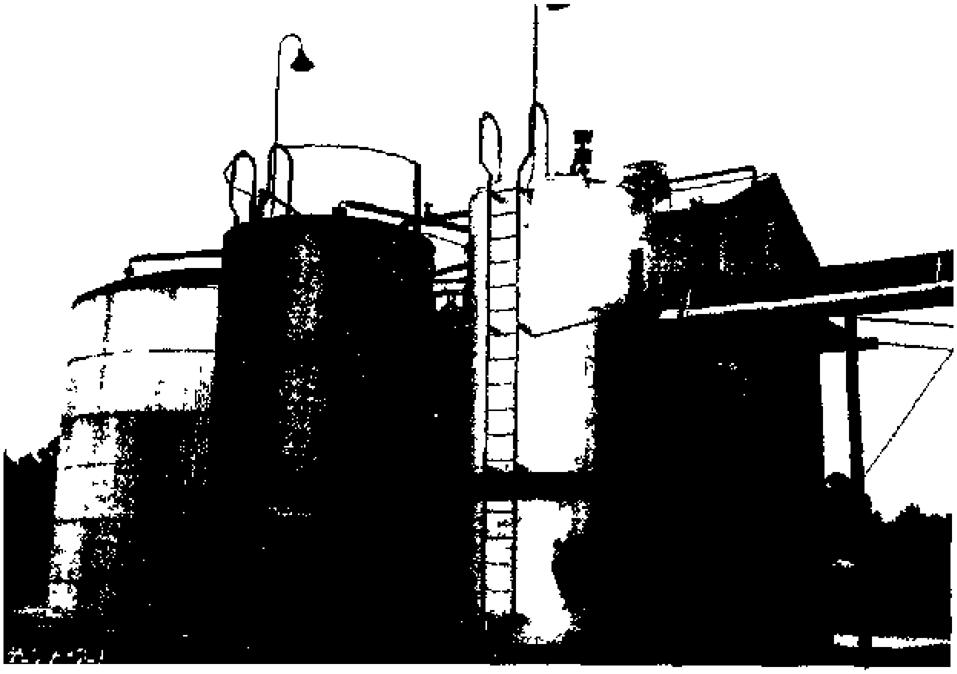

Figure 21. Methanol shift tanks in front, formaldehyde interim storage in second row, blending building behind.

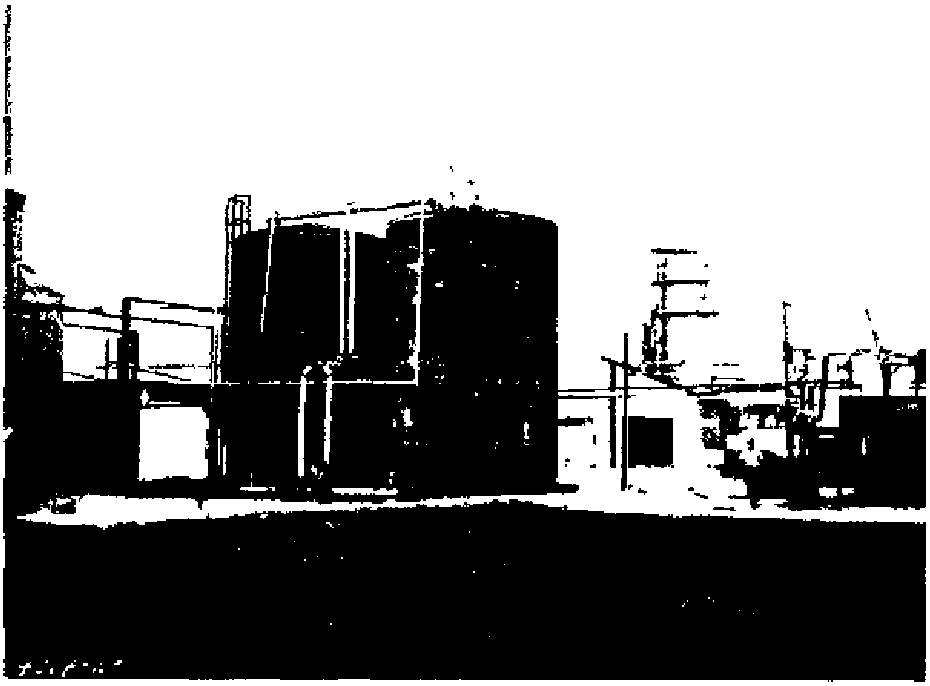

Figure 22. Formaldehyde storage and loading area. Can see scrubber on left of formaldehyde storage (bottom).

The interim storage tanks are located in the same diked area as the methanol shift storage tanks, adjacent to the blending building The tanks are grounded, are equipped with flame arrestors, and have internal steam coils to maintain storage temperature and formaldehyde solubility. No mixing except thermal mixing is in use The formaldehyde solution is returned to the distillation column using Goulds centrifugal pumps with John Crane single mechanical seals similar to those used in the absorber system. The tanks, which are maintained at about 50°C, are vented to a small water scrubber, which virtually eliminates the tank emissions.

The final product tanks are larger but similar to the interim storage tanks. Fifty percent formaldehyde solution, received from the distillation column, is stored at 50°C. This temperature is maintained by internal steam coils One tank has been fitted with a modified steam heating system which is mounted on the manhole cover for the unit (Figures 23 and 24). The system can be disconnected from outside the tank, then removed from the tank for

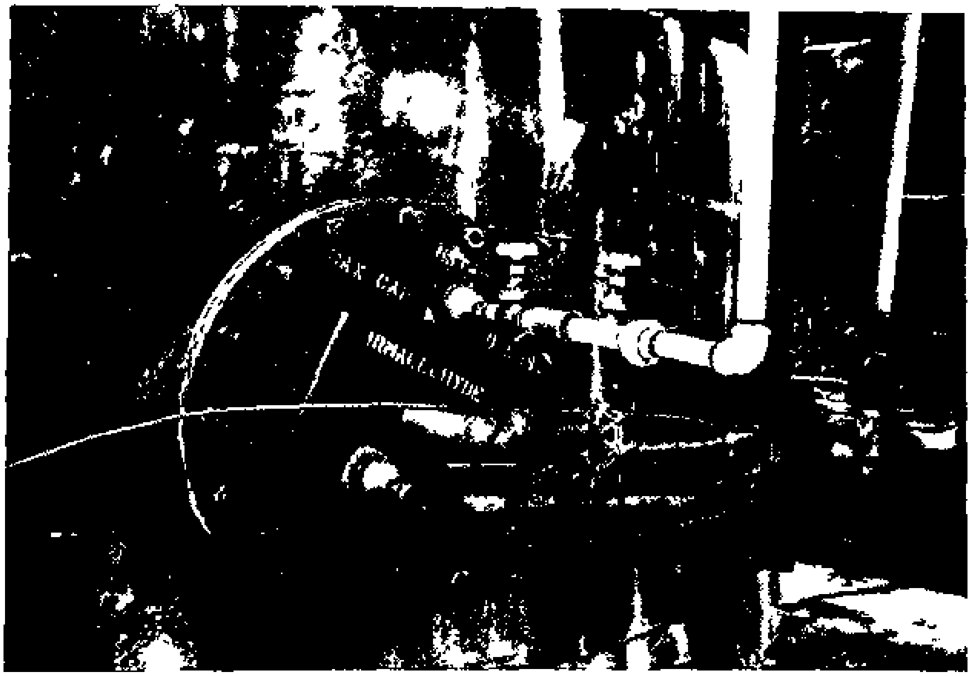

Figure 23. Formaldehyde storage tank manhole with steam lines attached.

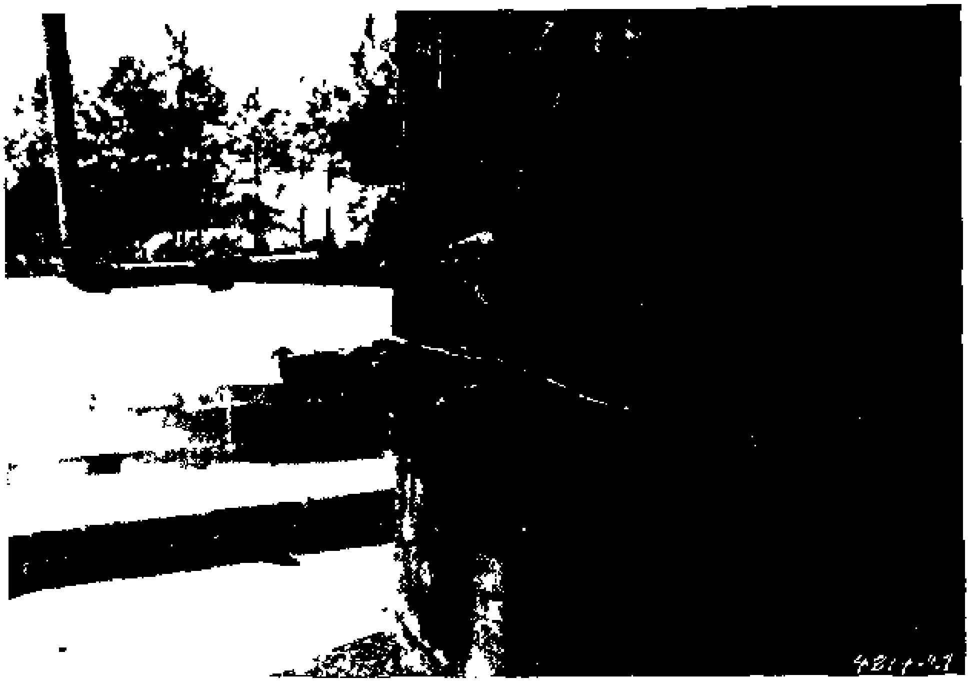

Figure 24. Formaldehyde storage tank manhole with steam lines attached.

repair This reduces the need for personnel entry into the tanks and also allows for adequate ventilation during repair. The two tanks are filled with formaldehyde and emptied on an alternating basis. This allows steam and water cleaning on a two week rotation. Water generated in the cleaning process is used as makeup water in the absorber system.

Emissions from all formaldehyde storage tanks including interim storage, final product storage, and blending are scrubbed in a passive scrubber hown in Figure 25 and schematically in Figure 26. The ventilation system for truck loading also uses this scrubber system. As the schematic shows, this is a very simple system consisting of a small scrubber tank, a drainage system, and a delivery system. The system works on the principle that as a tank is filled, the air above the liquid is forced out of the top of the tank by a pressure gradient. No other blower or vacuum system is needed. This system also works on thermal expansion or vapor

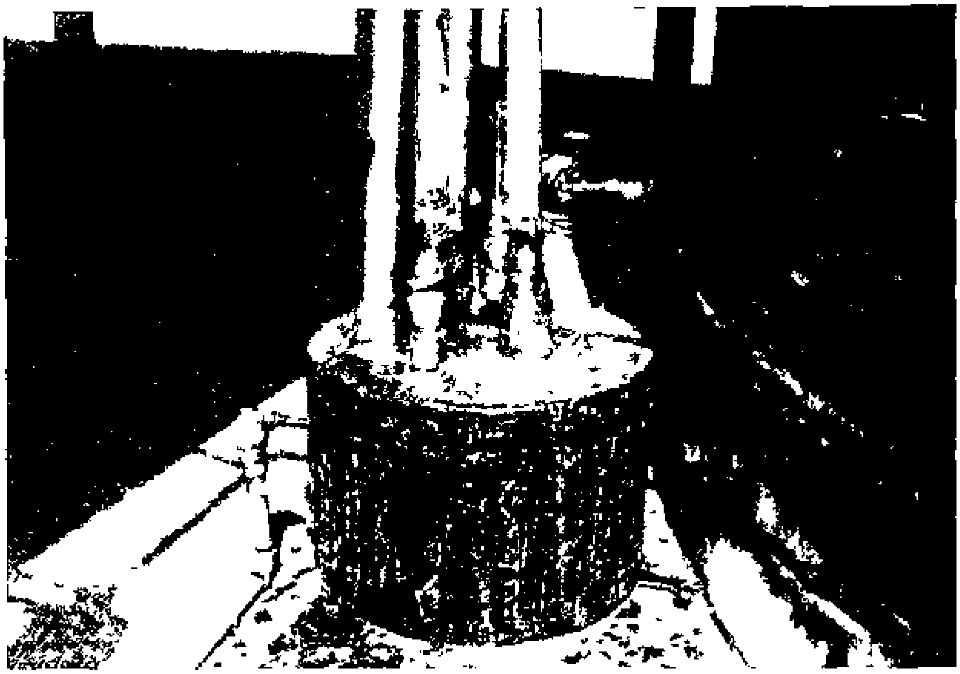

Figure 25. Formaldehyde emissions scrubber.

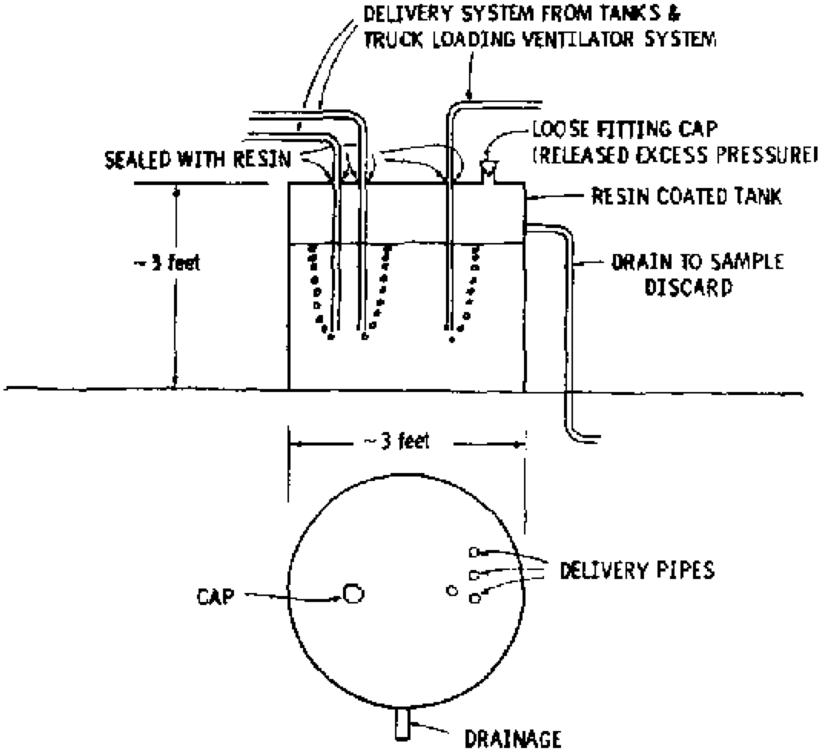

Figure 26. Schematic diagram of formaldehyde emissions scrubber.

pressure gradients. The released contaminate is air transferred to the passive scrubber by the delivery system. Inside the scrubber, the contaminated air is cooled by direct contact with water, which also captures the formaldehyde. A pressure drop of less than six inches can achieve the necessary scrubbing for several tanks. Water vapor from the contaminated air is sufficient to maintain the water level. Excess liquid, which averages about 0.3% formaldehyde, is sent to the sample discard station for reuse in the spray towers

This scrubber is an inexpensive method to reduce formaldehyde emissions from storage tanks. The tank and all lines were built by the plant staff from locally available material. Discussion with the plant manager indicate that the passive scrubber is effective in reducing noticeable emissions from the storage area.

7.7 BLENDING

The blending building (Figure 27) is an enclosed structure, which contains a tank equipped with an agitator on a large weighing scale Formaldehyde from the final product storage tanks is blended to meet the product specifications of consumers. The process operator is responsible for mixing and analyzing the product approximately once per day The blending pump, which provides mixing and also pumps the solution to the loading area, is a Gould's centrifugal pump with a John Crane seal with recirculated solution to lubricate the seal face. The top agitator uses a packed seal to prevent gaseous leaks into the building The tank is vented to the emissions scrubber described in Section 7.6.

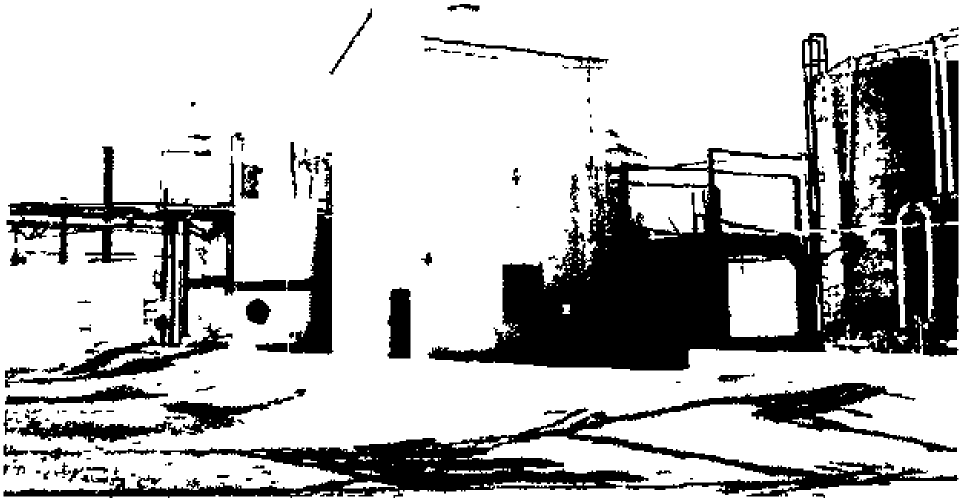

Figure 27. Blending building and formaldehyde storage.

7.8 FORMALDEHYDE LOADING

Formaldehyde is loaded into tank trucks and rail tank cars at the Hampton plant. Two separate loading areas, one each for rail and truck loading, are used as indicated in Figure 1. Formaldehyde is pumped from the blending pump to the area that is loading.

The truck loading area (Figure 28) is located adjacent to the formaldehyde storage tanks. Tank trucks are loaded using a top loading, swivel-jointed, dip tube shown in the storage position in Figure 29. A suction tube accompanies the dip tube when placed into the tank truck. This suction setup is rated at 600 cfm and transfers the captured emissions into the water scrubber described earlier. This ventilation appears effective, but not to the extent expected by the plant.

Tests of the equipment are included in the results section.

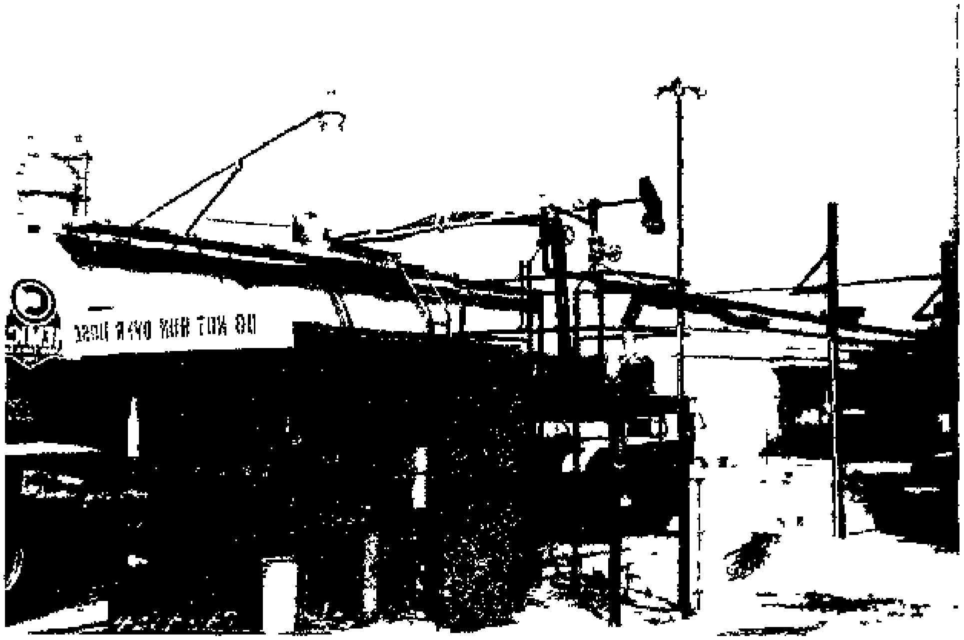

Figure 28. Formaldehyde loading area; scale in center.

Figure 29. Formaldehyde loading area.

Loading is metered according to weight. The operator is not in the loading area for the duration, but returns for periodic checks. The automatic delivery system shuts off the pump when the required load is delivered. This auto load mechanism prevents overfilling and reduces worker exposure.

A safety shower and eyewash are located at the bottom of the loading platform for emergencies.

The rail tank car loading area uses the same pump to load the tank cars that is used when loading trucks. These operations are similar, except no suction tube is present in the rail tank car loading area. Figure 30 shows the formaldehyde rail car loading area.

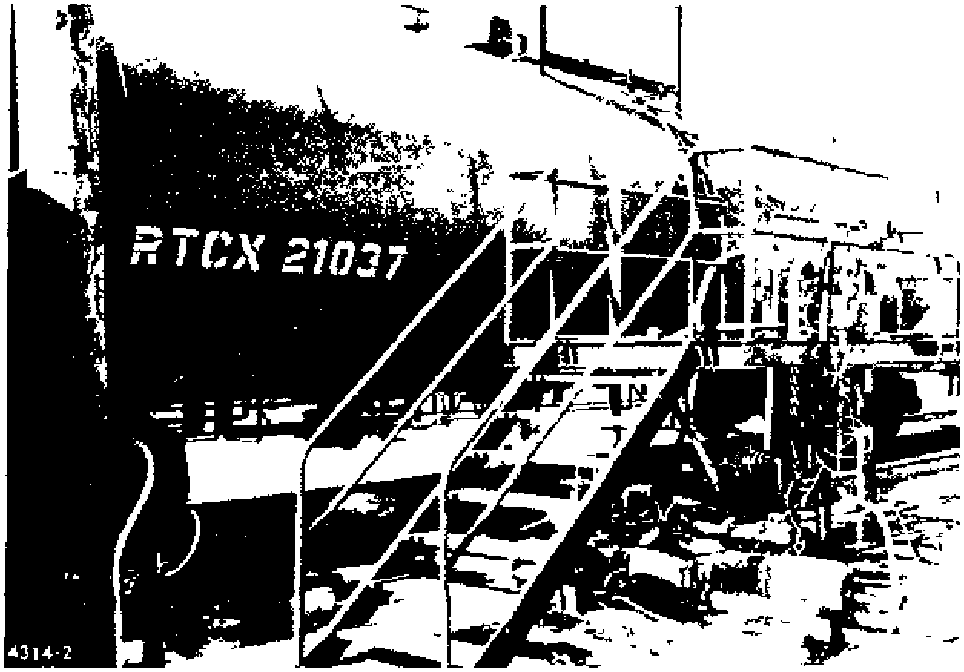

Figure 30 Formaldehyde rail car loading.

7.9 CONTROL ROOM

Operators spend 70-80% of their time monitoring the production operation from a control room inside the main office building. Critical operations can be monitored and controlled from this area and alarms alert operators to problems.

The control room is equipped with two local exhaust ventilation hoods (Figure 31) in which formaldehyde and methanol samples are analyzed. Formaldehyde samples are analyzed in the larger of the two hoods. Exhaust control for this hood is provided by an 18-inch propeller-type exhaust fan located at the top rear of the booth. This fan diverts air to a plenum and then to a flexible exhaust duct running horizontally to an outside wall of the building. The exhaust duct ends flush at the wall and air is exhausted outside through wall louvers approximately 10 feet above the ground.

Figure 31. Area sample control room. Methanol hood on right; formaldehyde hood on left; center, tripod.

Methanol samples are analyzed in a smaller hood (Figure 32). The exhaust control for this hood consists of a small fan pushing the air into a 6 inch by 3 inch duct that is exhausted through the roof of the building.

Figure 32. Methanol analysis hood; kitchen fan setup by door to office area, control room.

8. SAMPLING AND ANALYSIS

Two types of samples were collected: 1) long-term or time weighted average (TWA) and 2) short-term or STEL (short-term exposure level). Samples of both of these types were collected as personal samples or as area samples. All of these types of samples were collected to characterize both formaldehyde and methanol concentrations during this survey.

One process operator and two maintenance workers were sampled for formaldehyde and methanol for four and three days, respectively, to determine the average worker exposure during normal shift work. The process operator was also sampled during potentially high exposure activities for short-term exposure levels Ten areas frequented by the process operator were also sampled three times including two consecutive samples to determine general concentrations of formaldehyde and methanol in these areas. Six sources were sampled to estimate the contribution of these sources to the general formaldehyde and methanol area concentrations.

In order to ensure that the source samples represented the source emissions and were not affected by concentrations of the same pollutant in the surrounding area, or by dilution, each source sampled was wrapped tightly with clear plastic and tape-sealed as shown in Figures 33 and 34. The concentration levels in the source samples were assumed to correspond to the amount of agent released by the source over the sampling period and were expressed as the amount of pollutant released per day.

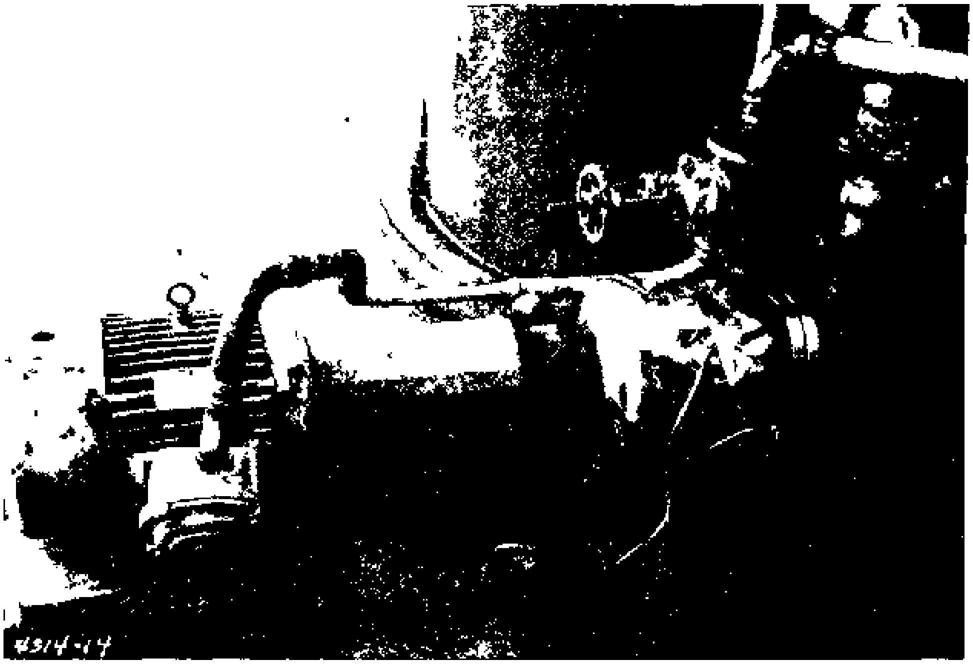

Figure 33. Second spray tower pump; wrapped; tubes in place.

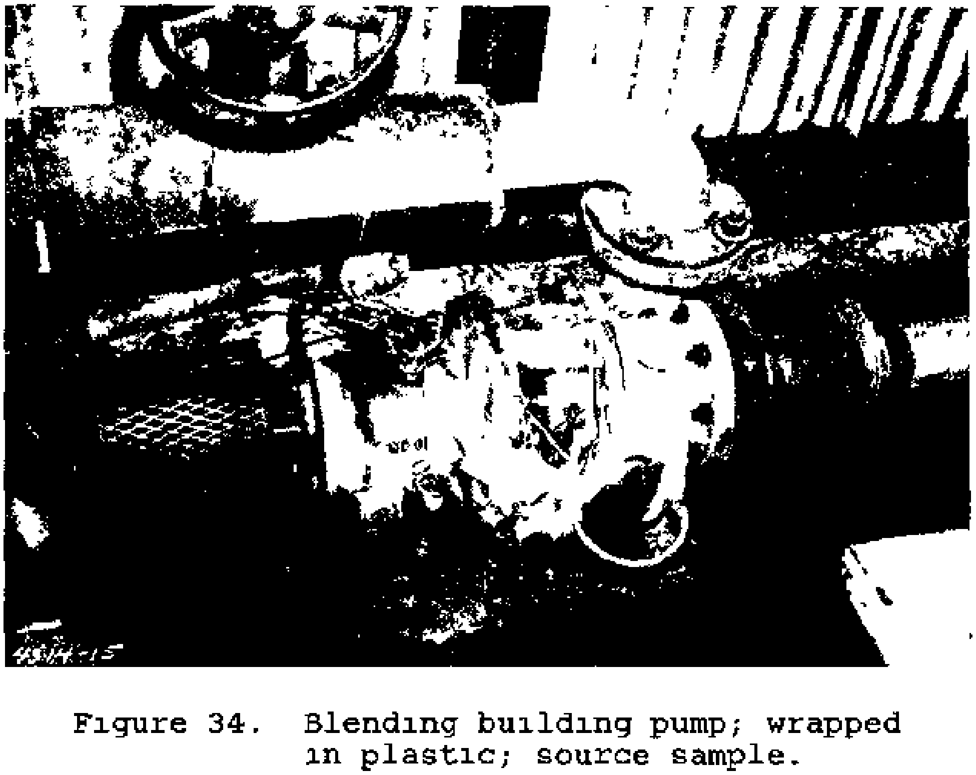

Figure 34. Blending building pump; wrapped in plastic; source sample.

8.1 SAMPLING TIME

The survey objectives dictated that two types of samples be collected. Long-term samples, collected over periods of 120 minutes or longer were used to determine time-weighted average exposures Short-term samples, collected over periods of between 15 and 120 minutes, were used to determine the exposures from certain, typically short events occurring during normal regular shift hours Long-term samples were generally comprised of two approximately 240-minute long consecutive sampling periods and were used to determine an eight-hour, time-weighted average according to the following formula:

$$TWA = \frac{T_1X_1 + T_2X_2}{T_t} \qquad \text{Ref. [1]}$$

where TWA = time-weighted average
T_1, T_2 = sampling times for long-term samples
X_1, X_2 = concentrations of long-term samples
T_t = total time

This same formula was applied to personal and area samples Personal long-term samples were repeated on a second day to enhance the survey results and to evaluate day-to-day variations and peak exposures

Short-term samples were taken during operator activities that were expected to produce peak exposures which would significantly contribute to and affect the results of long-term samples. Another reason for taking these samples was to indicate where controls may be most effective if the exposure concentration levels needed to be reduced. Short-term samples were taken at flow rates of about 200 cm^3/min (as compared with 100 cm^3/min for long-term samples) to assure collection of a pollutant volume sufficient for reliable analysis

8.2 SAMPLING METHODS

Sampling for formaldehyde was conducted using an active dosimeter method developd by the research department of Monsanto Agricultural Products Company [2] and approved by the NIOSH project officer, Mr. W. N. McKinnery, Jr. The method uses sampling tubes packed with 2,4-Dinitro-phenylhydrazine (2,4-DNPH)-coated silica gel to absorb formaldehyde from the sampled gas. To draw the gas through the tubes, MRC used DuPont Model P200 portable sampling pumps, which were calibrated and set to deliver a constant flow rate (±5%) of approximately 100 cc/min (actual pumps ranged from 92.6 to 107.5 cc/min) for long-term samples, as suggested by Mr. David Haile, supervisor of the MRC industrial-hygiene certified laboratory. Short-term samples were collected using the same pumps set and calibrated at a constant flow rate (±5%) of approximately 200 cc/min (actual pumps ranged from 193.8-210 5 cc/min). Pumps were checked for significant (greater than ±5%) deviation after use, and the samples were discarded when a significant deviation was observed.

To assure quality of results, formaldehyde sample blanks and spikes were used and all samples were analyzed and reported in accordance with standard MRC Quality Assurance/Quality Control procedures. Additional details on formaldehyde sampling and analysis methods are provided in Appendix B.

Sampling for methanol was conducted using a NIOSH-approved active dosimeter method, NIOSH 559. Silica gel tubes were used in conjunction with DuPont Model P200 pumps which were set and calibrated at a constant flow rate (±5%) of approximately 50 cc/min (actual pumps varied between 47.0-54.4 cc/min) for personal, source, and area sampling. Pump flowrates were checked after sampling to ensure constant flow

To assure quality of results, an unexposed silica gel tube was collected as a blank during each sampled shift. In addition, methanol samples were collected in duplicate and one of the duplicates was spiked during sampling with either 0.8 or 1.2 times the PEL to check on recovery and precision of sampling and analytical procedures. All methanol samples and blanks were analyzed according to MRC Quality Assurance/Quality Control Procedures. Additional details on methanol sampling and analysis procedures used are included in Appendix B.

During sampling, a log of pertinent information was developed using Monsanto DMEH Industrial Hygiene Monitoring Forms. Recorded information on these forms includes: tube identification number, identification of sampling location, pump initial and final flows, sampling time, and comments.

8.3 NUMBER OF SAMPLES

Excluding blanks and spiked blanks, 71 formaldehyde and 44 methanol samples were collected during the survey as shown in Table 1, Section 1.2.

8.4 LOCATIONS SAMPLED

Figure 35 shows the location in the plant where sampling was conducted. Table 2 lists the locations sampled and the number of area and source samples taken at that location.

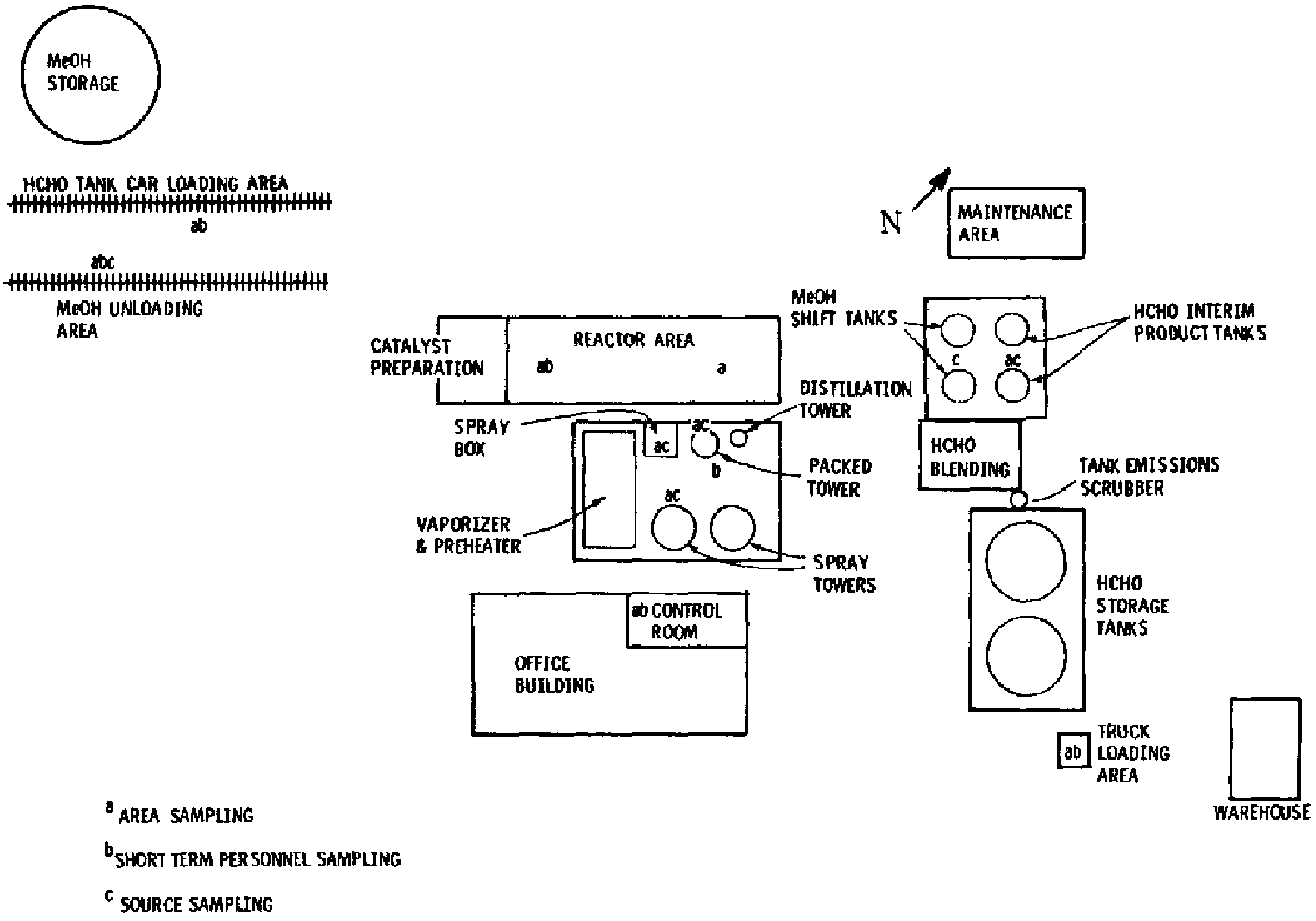

Figure 35. Locations of area, short-term personal, and source sampling conducted during the survey.

TABLE 2. AREA AND SOURCE SAMPLE NUMBERS AND LOCATION SUMMARY

Location	Number of samples	
	Formaldehyde	Methanol
Area		
Formaldehyde truck loading	1	
Formaldehyde tank car loading	1	
Spray box area	3	3
Distillation column area	3	3
Converter area - north end	3	3
Converter area - south end	3	3
Spray Tower #1	3	3
Control/lab room	6	4
Blending building	3	3
Control lab hood	4	1
Methanol shift tank storage	1	1
Methanol unloading		1
Source		
Formaldehyde interim product pump	2	2
Spray tower #2 pump	2	
Distillation column pump	2	
Blending pump	4	
Spray box pump - fluid sealed	2	
Spray box pump - nonfluid sealed	1	
Methanol unloading pump		1
Totals	44	28

9. RESULTS

The following tables present the analytical results for samples taken at the Reichhold Chemicals, Inc., Hampton, SC, plant during August 24-27, 1982. All volumes and concentrations have been corrected to standard temperature and pressure (20°C and 760 mm Hg). Tables 3 and 4 present the long-term personal sample analytical results for formaldehyde and methanol, respectively. Short-term personal formaldehyde sample analytical results are presented in Table 5. No short-term methanol samples were taken. Area sample results are presented in Tables 6 and 7. Source sample results can be found in Tables 8 and 9. Results from the ventilation tests on the formaldehyde loading ventilation and the control lab hoods are presented in a discussion following the tables.

All methanol samples taken during the survey had a methanol quantity on the back half of the tube greater than 25% of the quantity on the front half of the tube (except those with concentrations below the detection limit). This indicates potentially significant loss of material must be taken into account when comparing these samples with others. It is not known at this time whether these tubes were subject to methanol migration during storage prior to analysis, were significantly affected by humid conditions during the survey, or actually had breakthrough during sampling. Also to be noted are the small concentrations found on the tubes.

TABLE 3. LONG-TERM FORMALDEHYDE PERSONAL SAMPLE ANALYTICAL RESULTS

Description	Day	Shift	Tube number	Flow[a] rate, cc/min	Sample time, min	Adjusted[b] volume, (V), L	Concentration, (C), ppm	Consecutive sampling period, min	8-hr TWA, ppm	Average[c] ppm
Operator	8/24	1	1,782	100.0	184	17.72	0.56			
	8/24	1	1,270	100.0	175	16.85	0.61	359	0.58	
	8/25	1	19	96.8	250	23.52	0.57			
	8/25	1	1,868	96.8	194	18.25	0.82	444	0.68	
	8/26	1	1,809	98.0	243	23.60	0.50			
	8/26	1	1,312	98.0	195	18.94	0.65	438	0.57	
	8/27	1	1,758	102.0	238	23.94	0.29			
	8/27	1	1,321	102.0	186	18.71	0.50	424	0.38	0.55
Maintenance Worker 1 (Robertson)	8/24	1	1,204	101.3	175	17.07	0.13			
	8/24	1	1,103	101.3	172	16.78	0.51	347	0.32	
	8/25	1	1,055	100.7	245	23.95	0.20			
	8/25	1	1,156	100.7	200	19.77	0.08	445	0.15	
	8/26	1	1,886	101.4	235	23.62	BDL[d]			
	8/26	1	1,228	101.4	189	18.99	BDL	424	BDL	0.16
Maintenance Worker 2 (Shelly)	8/24	1	1,051	103.1	174	17.28	0.20			
	8/24	1	1,978	103.1	171	16.98	0.17	345	0.19	
	8/25	1	1,075	101.0	241	23.66	0.09			
	8/25	1	1,164	101.0	196	19.24	0.12	437	0.10	
	8/27	1	1,284	101.7	242	24.27	0.10			
	8/27	1	1,219	101.7	135[e]	13.54	0.19	377	0.13	0.14

[a] Flowrate was determined as follows: within ±5% deviation of calibration, assume initial flowrate, >5% but <15% deviation, average the 2 flowrates; >15% deviation, discard the sample.

[b] Adjusted to standard conditions - 68°F, 29.92 in Hg (20°C, 760 mm Hg).

[c] Average concentration = $(V_1C_1 + V_2C_2 + \ldots)/(V_1 + V_2 + \ldots)$

[d] Below detectable limit (0.05 ppm).

[e] Split time due to worker leaving plant site.

TABLE 4. LONG-TERM METHANOL PERSONAL SAMPLE ANALYTICAL RESULTS

Description	Day	Shift	Tube number	Flow[a] rate, cc/min	Sample time, min	Adjusted[b] volume (V), L	Concentration (C), ppm	Consecutive sampling period, min	8-hr TWA[c] average, ppm	Activity average ppm
Operator	8/24	1	01	48.4	184	8 58	>9.75			
	8/24	1	10	48.4	175	8 16	>6 58	359	>8 20	
	8/25	1	19	50 9	235	11.62	>3 73			
	8/25	1	25	50.9	194	9.59	>5 72	429	>4 63	
	8/26	1	34	51 5	243	12 40	>6.84			
	8/26	1	44	51.5	195	9 95	>7 9	438	>7 31	
	8/27	1	55	50 6	239	11 92	BDL[d]		BDL[g]	>5 69
	8/27	1	63	50 6	186		VOID[e]			
Maintenance worker 1	8/25	1	17	52 2	245	12.43	BDL			
	8/25	1	26	52 2	200	10 15	BDL	445	BDL	
	8/26	1	35	52 7	235	12 27	BDL			
	8/26	1	45	52.7	189	9 87	BDL	424	BDL	BDL
Maintenance worker 2	8/25	1	18	48.2	241	11 29	1 66			
	8/25	1	27	48 2	196	9 18	1.36	437	>1 53	
	8/27	1	56	53 7	242[f]	12.82	BDL		BDL[g]	>1 33
	8/27	1	64	53 7	134[f]		VOID[e]			

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[a] Flow rate was determined as follows. within ±5% deviation of calibrate flow rate, assume initial flowrate, >5% but <15% deviation, average the 2 flowrates, >15% deviation, discard sample

[b] Adjusted to standard conditions - 68°F, 29 92 in Hg (20°C, 760 mmHg)

[c] Average concentration = $(V_1C_1 + V_2C_2 + \quad)/(V_1 + V_2 + \quad)$

[d] Below detectable limits (1 0 ppm)

[e] Void due to contamination

[f] Split time due to worker leaving plant site

[g] 4-hr TWA

TABLE 5. SHORT-TERM FORMALDEHYDE PERSONAL SAMPLE ANALYTICAL RESULTS

Description	Day	Shift	Tube number	Flow[a] rate, cc/min	Sample time, min	Adjusted[b] volume (V), L	Concentration (C), ppm	Activity[c] average, ppm
Formaldehyde truck loading - operator	8/24	1	1,192	193.8	61	11.38	0.55	0.55
Formaldehyde rail car loading - operator	8/26	1	439	202.7	100	20.09	0.19	0.19
Process sampling - operator	8/25	1	1,277	196.1	28	5.34	1.89	
	8/25	1	1,869	196.1	18	3.43	1.13	
	8/26	1	1,862	198.7	27	5.31	0.67	
	8/26	1	1,329	210.5	28	5.84	0.40	
	8/27	1	1,962	205.5	15	3.04	0.49	
	8/27	1	1,129	204.8	13	2.62	0.31	0.87

[a] Flow rate determined as follows: with ±5% deviation, assume initial flowrate, >5% but <15% deviation, average the 2 flowrates, >15%, discard sample.

[b] Adjusted to standard conditions - 68°F, 29.92 in. Hg (20°C, 760 mm Hg).

[c] Average concentration = $(V_1C_1 + V_2C_2 + \ldots)/(V_1 + V_2 + \ldots)$.

TABLE 6. FORMALDEHYDE AREA SAMPLE ANALYTICAL RESULTS

Description	Tube number	Flow[a] rate, cc/min	Sample time, min	Adjusted[b] volume (V), L	Concentration (C), ppm	Area[c] average, ppm
Formaldehyde truck loading area - 8 ft from truck hatch	1,338	206.4	49	9.74	8.62	8.62
Formaldehyde tank car loading area - 5 ft from rail car hatch	1,928	103.4	101	10.35	0.28	0.28
PRODUCTION AREA						
Spray box area - BZH - base of spray box - above transfer pumps	1,796	VOID - 39.3% flow deviation				
	1,850	102.7	206	20.98	0.14	
	1,238	102.7	241	24.54	0.16	0.15
Distillation column area - BZH - above recycle pumps	69	98.2	234	22.13	0.34	
	1,135	94.7	207	19.43	0.05	
	1,201	94.7	241	22.62	0.12	0.17
Converter area - north end - ~3 ft above floor - hot (120°F) area - walkway between reactors	1,840	98.8	239	20.98	0.17	
	07	107.5	209	22.28	0.19	
	1,708	107.5	244	26.00	0.22	0.20
Converter area - south end - ~3 ft above floor - hot (120°F) area - walkway between reactors	1,107	92.6	237	21.14	0.28	
	1,804	93.4	209	19.35	0.12	
	52	93.3	240	22.20	0.11	0.17
Spray tower #1 - (south) - BZH - above transfer pumps	1,918	100.7	235	22.79	1.38	
	1,022	98.4	207	20.19	0.23	
	1,314	98.4	237	23.22	0.16	0.60
Control/lab room - BZH - center of room	78	101.7	228	22.54	0.68	
	1,057	101.7	200	19.77	0.69	

(continued)

TABLE 6 (continued)

Description	Tube number	Flow[a] rate, cc/min	Sample time, min	Adjusted[b] volume, L	Concentration, ppm	Area[c] average, ppm
Control/lab room - BZH - center of room (continued)	1,884	101.7	246	24.80	0.64	
	56	101.7	185	18.65	0.52	
	1,808	99.3	241	24.58	0.44	
	280	99.3	177	17.33	0.38	0.56
Blending building area - 4 ft above floor - 8 ft from pump	1,920	101.7	109	10.76	0.27	
	1,120	101.7	246	24.29	1.02	
	1,957	98.4	130	12.61	0.40	0.69
Control/lab room hood area - ~2 in. from face of hood at BZH	1,230	200.0	25	4.96	0.65	
	1,286	209.4	20	4.13	0.44	
	1,144	209.1	12	2.38	BDL	
	1,812	208.3	12	2.47	1.14	0.57
MeOH shift storage/interim product storage area - BZH - center of area - 8 ft from HCHO interim storage return pump	1,023	103.4	232	23.66	0.12	0.12

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[a] Flow rate determined as follows: ±5% deviation, assume initial flowrate; >5% but <15% deviation, average 2 flowrates, >15%, discard sample.

[b] Adjusted to standard conditions - 68°F, 29.92 in Hg (20°C, 760 mm Hg).

[c] Average concentration = $(V_1C_1 + V_2C_2 + \ldots)/(V_1 + V_2 + \ldots)$.

TABLE 7. METHANOL AREA SAMPLE ANALYTICAL RESULTS

Description	Tube number	Flow[a] rate, cc/min	Sample time, min	Adjusted[b] volume (V), L	Area concentration (C), ppm	Area[c] average, ppm
Methanol unloading area - BZH - center of middle rail car - ~15 ft from hatch - directly opposite the discharge valve	05	51.6	285	14.05	BDL[d]	<1.0
Methanol delivery sample analysis - setup @ BZH in control/lab room - inside lab hood	06	51.5	44	2.18	51.41	51.41
Spray box area - BZH - base of spray box above transfer pumps - vaporizer ~8 ft away	09	51.8	225	11.29	BDL	
	39	47.0	203	9.46	BDL	
	50	47.0	241	11.23	BDL	<1.0
Distillation column area - BZH - above MeOH recycle pumps	14	54.3	235	12.42	BDL	
	40	49.3	205	10.02	1.53	
	49	49.3	242	11.83	BDL	>1.15
Converter area - north end - ~3 ft above floor - hot (~120°F) area - walkway between reactors	15	48.1	239	11.07	BDL	
	37	48.2	208	9.94	BDL	
	47	48.1	245	11.68	BDL	<1.0
Converter area - south end - ~3 ft above floor - hot (~120°F) area - walkway between reactors	08	49.6	237	11.33	1.11	
	38	51.1	208	10.54	BDL	
	48	51.1	244	12.36	BDL	<1.04

(continued)

TABLE 7 (continued)

Description	Tube number	Flow[a] rate, cc/min	Sample time, min	Adjusted[b] volume (V), L	Area concen- tration (C), ppm	Area[c] average, ppm
Spray tower #1 - south - BZH - above transfer pumps	13	VOID - 39.6% deviation from calibration				
	41	53.4	204	10.80	BDL	
	53	53.4	238	12.60	BDL	<1.0
Blending building - 4 ft above floor - 8 ft from pump	21	49.6	110	5.24	BDL	
	29	47.1	247	11.30	BDL	<1.0
	59	48.9	127	VOID[e]		
Control/lab room - BZH - center of room	36	50.3	246	12.26	5.5	
	46	50.3	186	9.28	8.65	
	57	51.8	241	12.31	BDL	<9.09
	65	51.8	177	VOID[e]		
Methanol shift storage/interim product storage area - BZH - center area - 8 ft from HCHO interim product pumps	62	48.2	225	10.70	BDL	<1.0

[a] Flow rate determined as follows: ±5% deviation, assume initial flowrate; >5% but <15% deviation, average 2 flowrates; >15%, discard sample.

[b] Adjusted to standard conditions - 68°F, 29.92 in Hg (20°C, 760 mm Hg).

[c] Average concentration = $(V_1C_1 + V_2C_2 + \ldots)/(V_1 + V_2 + \ldots)$.

[d] Below detectable limit (1.0 ppm)

[e] Void due to sample contamination.

TABLE 8. FORMALDEHYDE SOURCE SAMPLE ANALYTICAL RESULTS

Description	Tube number	Flow[a] rate, cc/min	Sample time, min	Adjusted[b] volume (V), L	Concentration (C), ppm	Average[c] concentration, ppm
Formaldehyde interim product pump (to distillation column) - wrapped in plastic - fluid sealed	36	94 8	176	16.21	50 9[d,e]	
	437	94 8	216	19.91	8.00	<27.3
Spray tower #2 pump - wrapped in plastic - fluid sealed	1,786	94.8	201	18.52	4.33	
	289	94 8	212	20 10	4.77	4 56
Distillation column pump - wrapped in plastic - nonfluid sealed	1,898	97.1	188	17.74	1.20	
	09	97.1	213	20.10	2 78	2.04
Blending pump - wrapped in plastic - fluid sealed	1,252	VOID - tube fell out of zone				
	1,904	97.5	64	6.06	193.9[d,e]	
	37	VOID - 48.3% flow deviation				
	1,058	99 0	133	12 99	<95.2[d,e]	<127
Spray box pump - fluid sealed	1,839	96.6	185	17.72	18.9	
	1,074	96.6	237	22.69	17 8	18.4
Spray box pump - nonfluid sealed	1,254	106 8	222	23 38	<55.2[d,e]	<55.2

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[a] Flow rate determined as follows: ±5% deviation, assume initial flowrate; >5% but <15% deviation, average 2 flowrates; >15%, discard sample

[b] Adjusted to standard conditions - 68°F, 29.92 in. Hg (20°C, 760 mm Hg).

[c] Average concentration = $(V_1C_1 + V_2C_2 + \ ..)/(V_1 + V_2 + \ ..)$.

[d] Breakthrough occurred on the tube

[e] Out of calibration range

TABLE 9. METHANOL SOURCE SAMPLE ANALYTICAL RESULTS

Description	Tube number	Flow[a] rate, cc/min	Sample time, min	Adjusted[b] volume (V), L	Concentration, (C), ppm
Methanol unloading pump - wrapped with plastic and duct tape	04	49.8	285[c]	13.67	32.03
Formaldehyde interim product pump - wrapped in plastic	24	51.1	158	7.84	11.72
	58	54.4	233	VOID[d]	

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[a] Flow rate determined as follows: ±5% deviation, assume initial flowrate; >±5% but >± deviation, average 2 flowrates; >±15%, discard sample.

[b] Adjusted to standard conditions (68°F, 29.92 in Hg)

[c] Unloading pump not started until 1245 (171 min).

[d] Void due to contamination of sample

9.1 FORMALDEHYDE LOADING

Local exhaust ventilation control is provided for tank truck loading; no forced ventilation control is provided for rail car loading. Prior to loading a tank truck, a 6-inch flexible exhaust duct is inserted into the hatch opening and positioned so that the end of the duct is approximately 6 inches below the hatch opening. Contaminated air is exhausted with the use of a centrifugal blower fan located at the loading platform. Air from the fan is directed through another section of 6-inch flexible exhaust duct to rigid PVC piping. Contaminated air is ultimately directed to the makeup water tank for the absorber.

The air velocity towards the exhaust duct was measured 4 inches from the duct face with an Alnor Jr., swinging vane velometer. Air velocity would have been measured directly at the duct face but the measurement was off-scale and could not be recorded. The velocity measured 4 inches from the duct was 225 fpm. In using the following formula, the air flow through the duct can be calculated:

$$Q = (10\ X^2 + A)V \qquad \text{Ref. [3]}$$

where V = centerline velocity at X distance from the hood, fpm

X = distance outward along axis in feet

Q = air flow, cfm

A = area of duct opening in square feet

The air flow for the duct is 294 cfm. In knowing that an average of 4,500 gallons of formaldehyde is loading into a truck over an average period of 40 minutes, one can determine the air within the tank which is displaced. Converting 4,500 gal to 602 ft^3, the the following volume of air is displaced per minute of loading:

$$\frac{602\ ft^3}{40\ min} = 15 \text{ cfm of air displacement}$$

It appears that the exhaust volume of 294 cfm should be more than adequate to remove displaced, contaminated air from the tank. However, condensing vapors assumed to contain formaldehyde gas were observed to be escaping the tank through the hatch opening during loading. This is possible since the air velocity at approximately one diameter in front of the hood (6 inches) is only approximately 7.5% of the velocity at the duct opening. In fact, the velocity towards the duct opening at a distance of 1/2 diameter (3 inches) directly to the side of the hood opening is only 7.5% of the velocity at the duct opening. Using the above formula of $Q = (10 X^2 + A)V$, one can determine the air velocity at the duct opening as 1,498 fpm, using the air volume (Q) as 294 cfm. Therefore, the velocity towards the duct opening at 3 inches to the side of the duct is only 112 fpm (7.5% of 1,498 fpm). Since the exhaust duct is lowered about 6 inches below the hatch opening, if the duct were in the middle of the opening, the distance from the edge of the duct opening to the open hatch edge would be approximately 11 inches. Capture velocity towards the duct at this point would be minimal. Thus, displaced contaminated air can escape the tank truck through the hatch since the capture velocity is not adequate at the hatch opening to collect it. These emissions could be reduced by capping the tank hatch, even partially.

9.2 CONTROL ROOM/LAB HOODS

9.2.1 Formaldehyde Analysis Hood

Ventilation measurements were taken with an Alnor Jr., swinging vane velometer to determine the average inward face velocity of the booth. Ventilation readings ranged from a positive pressure (air blowing out) at the left side of the booth face to 25 fpm inward on the right side.

Hood exhaust control is inadequate. With air blowing out of the left side of the booth, contaminated air is blown into the room, increasing the exposure for the operator during analysis. An inward air flow should exist across the entire face of the hood, with the inward air flow averaging a minimum of 100 fpm.

9.2.2 Methanol Analysis Hood

The boiling point is determined for all methanol samples, drawn from rail cars to be unloaded, within the smaller of two locally exhaust-ventilated laboratory hoods in the control/lab room. A smoke tube air flow test indicated that air is blowing out of the hood at the top right corner of the face. Air velocity measurements taken at the remainder of the hood face with an Alnor Jr., swinging vane velometer ranged from 0 to 50 fpm.

Hood exhaust control is inadequate. This is indicated by the very high methanol concentration measured with the area sample (number 6), probably caused by the air blowing out of the hood. An inward air flow should exist across the entire hood face. The inward air velocity should average a minimum of 100 fpm so as to provide adequate control during analysis.

10. CONCLUSIONS

10.1 FORMALDEHYDE EXPOSURE

10.1.1 Operator Long-Term Exposure

Two consecutive personal samples were taken on the same operator during the day shifts of Tuesday through Friday. The total sample period for each set of consecutive samples taken during a shift ranged from 359 to 444 minutes. The time-weighted average results for these sample periods should give a good estimate of the operator's daily 8-hour shift exposure. The sample results for each pair of samples have been averaged to yield a time-weighted average exposure concentration for each day the operator was sampled. The results are presented in Table 3, Section 9.

The four time-weighted average (TWA) concentrations for the four shifts sampled ranged from 0.38 to 0.68 ppm. The four TWA exposure concentrations are 23% or less of the OSHA TWA permissible exposure limit (PEL) of 3 ppm. Thus, the long-term operator exposure is considered to be nonexcessive and controlled for these days when the exposure was evaluated.

10.1.2 Maintenance Personnel Long-Term Exposure

Long-term samples were taken on each of the same two maintenance workers during each day shift of Tuesday and Wednesday; samples were taken on one of them on the Thursday day shift and on the other on the Friday day shift. Two consecutive long-term samples were taken on each maintenance worker during a shift. The total periods for each shift ranged from 345 to 445 minutes. A time-weighted average exposure concentration has been determined for each pair of consecutive samples worn. Each time-weighted average concentration should give a good estimate of a maintenance worker's exposure for an entire 8-hour shift. The sample results are presented in Table 3, Section 9.

The six time-weighted average exposure concentrations ranged from a nondetectable concentration (<0.05 ppm) to 0.32 ppm. All of these exposure concentrations are much less than (11% or less) the OSHA TWA PEL of 3 ppm and indicate a nonexcessive, controlled exposure for those maintenance workers and specific shifts sampled.

The maintenance workers were either cutting strands of silver to be used as the catalyst, installing a transformer, trimming the grounds, or mopping the floors at the beginning of the shift with a weak ammonia solution. Thus, although the workers were located in the area of the production unit and the control/lab room, they were not exposed to more potentially hazardous sources, such as repairing formaldehyde leaks or working on the actual process. If process-related maintenance activities were being conducted, such as repairing pumps or seals, the exposure levels may have been different, or even excessive. When major leaks are being repaired, a full-face gas mask is worn, which should provide adequate protection for such an intermittent exposure.

10.1.3 Formaldehyde Loading

One short-term personal sample was taken on an operator while loading a tank truck and one on an operator while loading a rail car. These results are reported in Table 5, Section 9. In addition, two area samples were taken at the railcar loading platform and at the tank truck loading platform while formaldehyde was loaded. The concentrations for these samples (0.28 ppm and 8.62 respectively), are presented in Table 6, Section 9.

Both the tank truck and rail car were loaded with 50% formaldehyde solution at 160°F (71°C), which is the most concentrated formaldehyde loaded at the plant and presents the most potentially hazardous exposure during loading. Neither of the personal samples exceeded the OSHA ceiling limit of 5 ppm.

The highest personal exposure concentration of 0.55 ppm is only 11% of the limit. These results indicate a controlled exposure for the samples taken. It should be stated that the sampling team would have liked to have taken more samples to more adequately evaluate the exposure, but only one tank truck and one rail car were loaded during the 4-day survey.

The worst exposure sources for the operator when loading are during sample withdrawal, when removing the loading line and exhaust duct, and when closing the hatch after loading. As stated in Section 7, local exhaust ventilation control is provided during tank truck loading. Although exhaust control is provided, it is not adequate. One could see formaldehyde mist condensing above the hatch during loading. In fact, the industrial hygienist sampling team member stood on the elevated loading work platform during loading and smelled the escaping formaldehyde gas, and experienced burning eyes due to the exposure. The personal sample result indicates that although exhaust control is inadequate, the operator was not exposed to escaping formaldehyde gas long enough during sample withdrawal to produce an excessive exposure.

When the loading had ceased, much less formaldehyde gas is escaping the hatch during line removal and hatch closing, since residual gas is not being forced out of the tank due to displacement during loading. Again, the sample result indicates that the operator is not exposed to an excessive formaldehyde concentration during these operations.

In summary, the operator is in the loading area such a short time that his exposure is not excessive.

Since rail car loading is performed without local exhaust ventilation control, it would be expected that the operator's exposure to formaldehyde gas would be greater than the exposure during tank truck loading. The personal sample result taken during rail car loading does not support this hypothesis. It is assumed that the operator was not exposed to high concentrations of formaldehyde gas escaping from the rail car dome during sample withdrawal, loading line removal, and dome closing for a long enough exposure time to create an excessive exposure.

During a different sampling period, weather conditions might be such that formaldehyde gas escaping from the dome would be blown at the operator while taking a sample, or during loading line removal and closing of the dome. It is possible that this condition might cause an excessive short-term exposure.

10.1.4 Formaldehyde Solution Sample Withdrawal and Analysis

10.1.4.1 Absorber/Distillation Column Sample Analysis-- Six short-term personal samples were taken on an operator while either 1) consecutively withdrawing an absorber and a distillation column sample and analyzing them or 2) withdrawing a single absorber or distillation column sample and analyzing it. The results of these samples are presented in Table 5, Section 9.

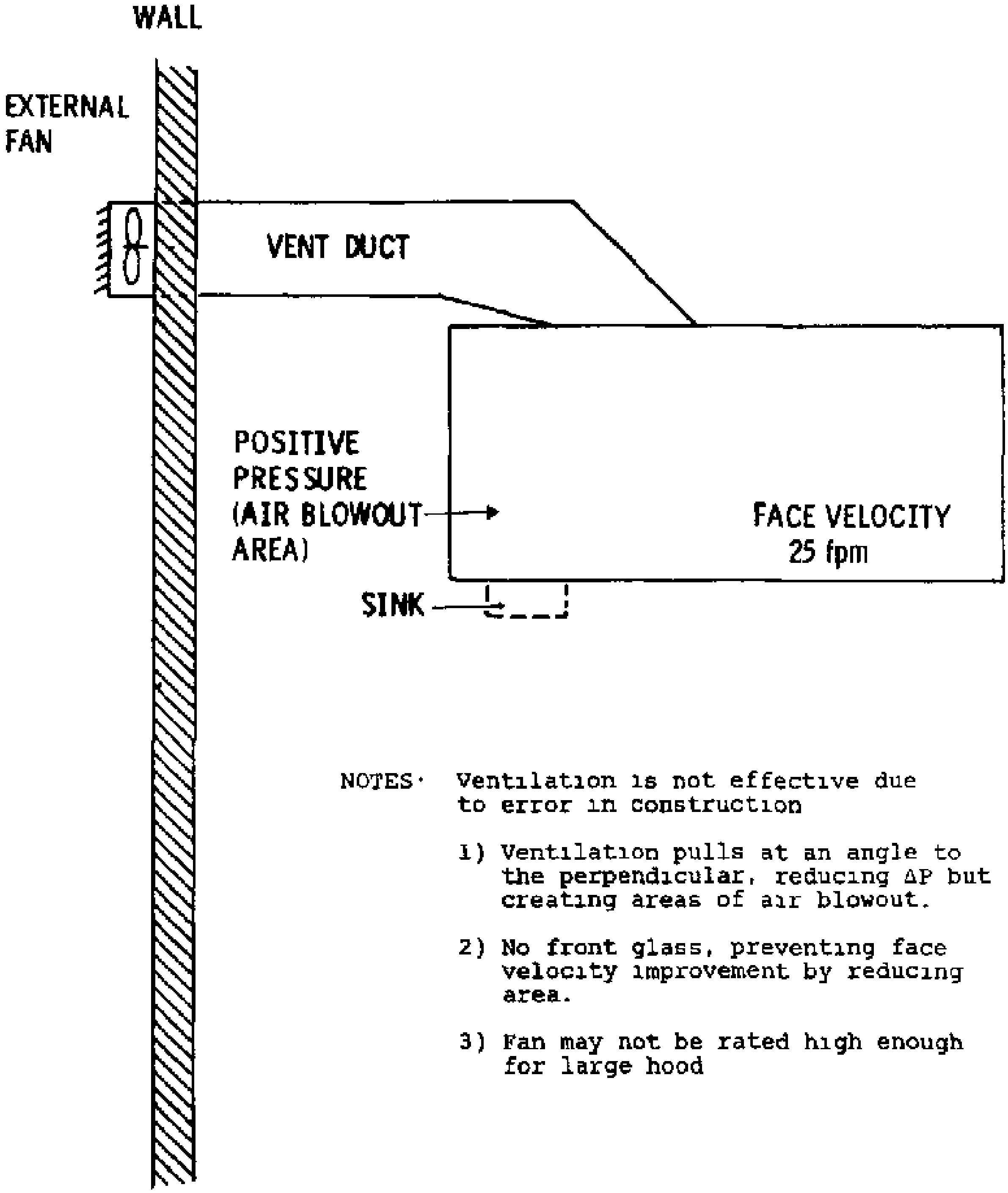
The six sample results range from a concentration of 0.31 ppm to 1.89 ppm. The highest concentration is 38% of the OSHA ceiling limit of 5 ppm, with all other sample concentrations only 23% or less of the OSHA ceiling limit. One would expect the sample results for two samples analyzed consecutively to be greater than those results for one sample analyzed. This did not occur, most probably due to varying weather conditions, slightly varying work procedures, etc., as well as the low levels of formaldehyde detected.

As stated in Section 8, the laboratory hood in which all process samples are analyzed, does not provide adequate local exhaust ventilation control. A diagram of this hood is shown in Figure 36. Since a positive pressure exists on the left side of the hood, contaminated air blows out of the hood, increasing the exposure to operators and other workers present inside the control room. Inward air flow at the rest of the hood face is far below a minimum recommended average velocity of 100 fpm. An increase in the inward face velocity of the hood to a minimum average of 100 fpm would increase control of formaldehyde gas during analysis, thus decreasing the operator's overall exposure during sample withdrawal and analysis.

10.1.4.2 Tank Truck or Rail Car Sample Analysis; Blend Tank Sample Withdrawal and Analysis--

It was not possible to take short-term personal samples on the operator during tank truck sample analysis or blend tank sample withdrawal and analysis due to limited amount of shipment during the time of the survey visit.

The greatest source during tank truck or rail car sample withdrawal and analysis would be the exposure resulting from sample withdrawal. Since local exhaust ventilation control is provided during tank truck sample withdrawal, one would expect the exposure while withdrawing a sample from a tank truck to be less than that when withdrawing a sample from a rail car. Although the operator exposure was quite low for withdrawal and analysis of a sample from a rail car (0.19 ppm), it could be higher if the wind is steadily blowing formaldehyde gas from the open dome in the direction of the operator during sample withdrawal. Adequate local exhaust ventilation control during rail car loading and sample withdrawal would insure greater exposure control.



NOTES: Ventilation is not effective due to error in construction

1) Ventilation pulls at an angle to the perpendicular, reducing ΔP but creating areas of air blowout.

2) No front glass, preventing face velocity improvement by reducing area.

3) Fan may not be rated high enough for large hood

Figure 36. Diagram of laboratory hood.

Again, due to insufficient time, it was not possible to evaluate the operator's exposure through a personal air sample when taking a blend tank sample and analyzing it. The blending tank sample required less than three minutes to take and the sample is analyzed at the customer's plant. It is expected that the exposure would be similar to that when taking an absorber or distillation column sample and analyzing it. Samples are taken in the same manner. Both types of samples are analyzed identically. Considering these similarities and the nonexcessive sample results in Table 5, Section 9, for the three samples taken on an operator during withdrawal of an absorber or distillation sample and analysis of that sample, the taking and analysis of blend tank samples would most probably present a nonexcessive exposure.

10.1.5 Formaldehyde Area Sampling

Two consecutive four-hour area samples were taken in seven locations in the plant. A third four-hour sample was taken on a second day at six of the locations, and additional consecutive samples were taken at the seventh location. Single samples were taken at three locations, and several short-term samples were taken at one location. One sample was voided due to extreme flow deviation of the pump. Long-term sample times ranged from 101 to 246 minutes and from 355 to 453 minutes for the two consecutive periods. Table 6 in Section 9 presents the analytical results of this sampling. The sample sites and sampling times were selected to give a representative indication of area formaldehyde concentration within the plant.

The five production area samples range from 0.05 to 1.38 ppm. The highest concentration is 46% of the OSHA permissible exposure limit of 3 ppm TWA. Area time-weighted averages for all samples taken in an area range from 0.15 to 0.69 ppm, or less than 23% of the permissible level.

The results of this area sampling indicate that the engineering controls and natural ventilation of the production area were adequate to prevent excessive exposure to workers while in these areas during the periods sampled.

As part of the area sampling, three consecutive long-term area samples were taken in the control/lab room on each of the 8/25, 8/26, and 8/27 day shifts, in order to determine the general TWA concentration within this room during the day shift. The total sampling periods for each set of samples ranged from 418 to 431 minutes, approximately seven hours total. The averages of each set of consecutive sample results ranged from 0.41 to 0.68 ppm, which should give a good estimate of the average room area concentration during these shifts. These results indicate that cross-contamination from the outside production process, plus that from formaldehyde sample analysis within the room, do not cause excessive concentrations in the room on an average, during the shift. Data on the results are presented in Table 6, Section 9.

Four short-term area samples were taken at the large laboratory hood in the control/lab room during formaldehyde sample analysis. The samples were located one foot to the right of the left sink within the hood and two inches outside of the hood. The results ranged from a below-detectable concentration (0.05 ppm) to 1.14 ppm, and are presented in Table 6, Section 9. Sample 1,230 (0.65 ppm) and sample 1,812 (1.14 ppm) gave greater sample concentrations than the corresponding personal samples worn by the operator during sample withdrawal and analysis (#1,329: 0.40 ppm; #1,129: 0.31 ppm), even though area sample periods were only slightly longer than personal sample periods. These higher concentrations inside the hood than outside of it indicate that laboratory hood local exhaust ventilation control is inadequate since the concentrations inside of the hood, which should be immediately diluted and removed, exceed those of the personal samples. Since ventilation measurements indicated air blowing out of the left side of the hood face, it is possible that contaminated air was being blown past the area samplers, increasing their concentration, without greatly contaminating the personal sample worn by the operator.

A short-term sample was also taken at the truck loading area during loading. The sample was located on the elevated platform used by the operator during loading preparation and ran for 49 minutes. A concentration of 8.62 ppm was found during this sample period, indicating that the local exhaust ventilation for the loading operation is not effective and should be reanalyzed by the plant. The ventilation duct should be inspected for leaks and the blower should be certified as vapor proof. This concentration exceeds the acceptable short term exposure limit and may indicate considerable exposure for workers in the area.

10.1.7 General Conclusions on Formaldehyde Exposure

The personal and area samples taken during the detailed industrial hygiene survey yielded exposure or potential exposure up to 46% of the OSHA PEL of 3 ppm TWA for long-term samples. A single short-term sample yielded 172% of the 5 ppm short-term TWA PEL, with all other samples yielding less than 38% of the OSHA PEL. Forty-two of the 48 samples were below 17% (0.5 ppm and 0.85 ppm) of the respective permissible levels.

All samples except the single truck loading sample indicated nonexcessive, controlled exposures for those days sampled. The exposure could be excessive for the operator while withdrawing and analyzing a sample from a rail car, although a long-term personal sample and short-term sample worn by the operator during rail car loading did indicate nonexcessive exposures. Different weather conditions, such as if the wind is blowing escaping formaldehyde gas from the open dome towards the operator during sample withdrawal, may produce an excessive short-term exposure.

The exposure for maintenance personnel could perhaps be excessive during major leak repair without protective gear. However, the wearing of proper personal protective equipment would be considered adequate control during such irregular, intermittent exposures.

10.2 METHANOL EXPOSURE

10 2.1 Operator Long-Term Exposure

Two consecutive personal samples were obtained for the same operator during each day shift from Tuesday through Friday. The total sample period for each set of consecutive samples worn by the operator ranged from 359 to 438 minutes, an approximate 6-hour to over 7-hour sampling period. A time-weighted average concentration was determined for each shift sampled, using the results for each set of samples worn. The time-weighted average concentrations should give a good estimate of the operator's exposure for each shift sampled. The results are shown in Table 4, Section 9.

Samples taken during the second half of 8/27 were apparently contaminated during analysis. All samples from that period, including a sealed blank, were analyzed separately from the other analyses and had very high methanol concentrations, indicating significant contamination. As a result, the time-weighted average concentration for the operator's second personal sample on 8/27 is not reported or used in this discussion.

The time-weighted average concentrations for each set of samples ranged from >4.63 to >8.20 ppm, which are 8% or less of the OSHA TWA PEL of 200 ppm. These results indicate a nonexcessive, controlled exposure during the times that these samples are taken.

10.2.2 Maintenance Personnel Long-Term Exposure

Two consecutive personal samples were taken on each of two maintenance workers during the day shifts of 8/25. Consecutive personal samples were also collected on one of these workers on the 8/26 day shift and for the other on the 8/27 day shift. The second sample of the set worn on 8/27 was apparently contaminated during analyses as explained earlier. Thus, this result will not be used in calculating a time-weighted average for that sample. The total sample period for each set of samples for maintenance workers ranged from 424 to 445 minutes, each set being more than a seven-hour sample period. It is felt that the time-weighted average of each set of sample concentrations should give a good estimate of the worker's exposure for that shift.

The time-weighted average concentration for each set of samples ranged from below detectable limits up to >1.53 ppm. These results are 0.8% or less of the OSHA TWA PEL, indicating a controlled, non-excessive exposure for those samples taken.

As explained in Section 10.1.2, the maintenance workers were not directly exposed to potential methanol vapor sources during sampling, such as during leak repair, process equipment maintenance, etc. It is expected that their exposure concentration would be higher if performing process maintenance. However, it should not be excessive since large spills would not be expected and the allowable exposures for methanol are relatively high.

10.2.3 Area Methanol Sampling

Two consecutive 4-hour area samples were taken in six locations in the plant. A third sample was taken on a second day at five of these locations and a second set of consecutive samples were taken at the control room. Four locations had individual samples taken. Sample times for individual samples ranged from 44 to 285 minutes and from 357 to 453 for the two consecutive samples. The 44-minute sample was for a short-term operation. The total sample times represent a good estimate of a shift, and analytical TWA results should be representative of concentrations present at these particular locations during the sampling period. Analytical results can be found in Table 7, Section 9.

Production area samples (five locations) range from below detectable limits (<1 ppm) to 1.53 ppm. This represents 0.8% or less of the OSHA PEL for methanol of 200 ppm.

Twelve of the 15 samples taken in the production area were below detectable limits, indicating an extremely low exposure potential to methanol in this area. The methanol unloading sample also is below detectable limits, indicating very low exposure potential in this area.

Two consectuive long-term area samples were taken in the control/lab room on 8/26 and 8/27 in order to determine the TWA exposure within this room. The second sample taken on 8/27 has been contaminated, similar to the others taken during that period, so that the TWA concentration for this day cannot be determined.

The TWA concentration for the two samples taken on 8/26 is greater than 6.9 ppm. The total sampling period was 432 minutes. It is expected that this sample concentration is a good estimate of the general area exposure witin the control/lab room during the day of sampling. This would indicate a nonexcessive general exposure within the control/lab room, since the exposure concentration is only 3.5% of the OSHA TWA PEL. Although only one day was adequately sampled, it is expected that the general room exposure should be nonexcessive at all times, since almost all of the other methanol sample results are quite low.

One short-term area sample was taken next to the smaller laboratory hood during the boiling point determination of a methanol sample. The sample concentration of 51.4 ppm indicates a relatively high exposure, though still below OSHA standards. This is most probably caused by contaminated air was blowing out of the hood at the right upper corner of the face across the sample. Although the exposure for the area sample was relatively high, the operator's long-term exposure is nonexcessive (#01; #10) since he does not analyze samples for a long period of time and contaminated air blowing out of the laboratory hood is not continuously blowing on the operator.

10.2.4 General Conclusions on Methanol Exposure

The personal samples indicate a very low, controlled methanol exposure. Maintenance personnel could be exposed to an excessive methanol exposure during major leak repair, but the proper wearing of protective equipment will provide adequate control during this intermittent, emergency-type exposure. Area samples also indicate very low concentrations, supporting the conclusion that the workers are protected in a well-controlled workplace.

10.3 EVALUATION OF ENGINEERING CONTROLS

10.3.1 Formaldehyde Sampling

Table 8 in Section 9 presents the analytical results of the source formaldehyde sampling. Footnotes indicate that 4 of the 11 samples taken had breakthrough into the backup section of the sample tubes. This breakthrough was greater than 25% for these four tubes, indicating that the sampling volume was too large or that the formaldehyde concentration from the sources were too high, and that these values can only be used as rough "minimum" estimates of any values. In addition, these samples exceeded the calibrated range for the method and the calibration curve was extrapolated to provide numerical results. Thus, these four samples are not indicative of the true concentrations for these sources, except to indicate very high concentrations compared to personal or area samples.

Six process pumps were sampled during the survey. These pumps use John Crane seals on Gould centrifugal pumps. Two types of sealing methods were studied, one type using recirculated fluid on the seal face, the other not using any liquid on the seal face. Four pumps used the fluid sealed face. Concentrations from these pumps ranged from 4.33 to >193.9 ppm indicating a significant difference in the performance of the seals. It should be noted, however, that as the formaldehyde concentration of the solution being pumped increases; i.e., from weak formaldehyde solution from the second absorber to the strong (50%) solution at the blending pump, the sample concentration also increases. The two nonfluid seal pumps sampled had concentrations from 1.20 to 55.2 ppm. Again, this is a large difference. However, the problem of stronger concentrations releasing more formaldehyde does not exist. It appears from the results of the sampling that there is not a large difference between fluid and nonfluid sealed pump release rates. The plant maintenance personnel do not replace nonfluid seals on a more regular basis than fluid seals, which seems to indicate no significant advantage of one type of seal over another.

Analytical results for mass released per day are summarized in Table 10. These results assume that the concentration released was constant within the volume sampled, and that the leak rate from the controls is constant.

TABLE 10. FORMALDEHYDE MASS LOADINGS RELEASED FROM SAMPLED ENGINEERING CONTROLS

Description	Tube no.	HCHO mass, µg	Sampling time, min	Daily release rate, g/d
Fluid sealed				
Spray tower #2 pump	1,786	98.42	201	7.05×10^{-4}
	289	117.7	212	8.00×10^{-4}
Spray box pump	1,839	411.1	185	3.20×10^{-3}
	1,074	495.1	237	3.01×10^{-3}
Interim product pump	36	>1,010[a]	176	$>8.33 \times 10^{-3}$
	437	195.5	216	1.30×10^{-3}
Blending pump	1,904	>1,440[a]	64	$>3.24 \times 10^{-2}$
	1,058	>1,520[a]	133	$>1.64 \times 10^{-2}$
Non-fluid sealed				
Spray box pump	1,254	>1,580[a]	222	$>1.03 \times 10^{-2}$
Distillation pump	1,898	26.08	188	2.00×10^{-4}
	09	68.68	213	4.64×10^{-4}

[a] Breakthrough occurred.

These samples indicate a low release rate, less than 0.025 kg/year, from each of these pumps. If a comparison of the two types of seals is made (in particular, comparing the two spray box pumps which pump the same material), the nonfluid seal appears to have a leakage rate a factor of 3 greater than the fluid seal. However, this is not supported when comparing the distillation pump and the blending pump which pump similar solutions. In this case, the blending pump (fluid seal) has a leakage rate which is a factor of 100 greater than the nonfluid seal. The comparison of the two seals indicates that other factors such as maintenance, length of use, and intermittent use also influence leakage rates.

10.3.2 Methanol Sampling

Table 9 in Section 9 presents the analytical results of the source methanol samples. It should be noted that breakthrough to the back section occurred on all three samples taken during the survey due to unknown causes. The analyst does not believe that this is the result of overloading of the tube, but rather, was due to migration or humidity problems. Three samples were analyzed for two pumps. One of these samples was voided due to contamination. Results of the remaining two samples indicates that the John Crane seals used were very effective, controlling release rates to 1.45×10^{-3} g/d for the methanol unloading pump and 5.50×10^{-4} g/d for the formaldehyde interim product pump. These values indicate that the methanol release rate is well controlled for these pumps sampled.

10.3.3 Laboratory Hoods

The two laboratory hoods in use are not adequate to capture volatile emissions during sample analysis. Redesign of the hoods appears necessary. Ventilation readings for the large hood registered as air blow-out (positive pressure) to 25 fpm, which is below the recommended minimum of 100 fpm inward velocity across the hood face.

The smaller hood was also tested and inward face velocities ranged from 0 to 50 fpm, also below the recommended face velocity. The insufficient face velocities allow contaminated air to be circulated into an area where the operator spends 70-80% of his time This circulation of contaminated air is supported by the area samples taken in the control room during the survey.

10.4 FINAL CONCLUSIONS

The Reichhold Chemicals, Inc., formaldehyde plant in Hampton, SC, uses work practices, engineering controls, and natural ventilation to control worker exposure to formaldehyde and methanol to acceptable levels. In most cases, formaldehyde exposure is below 20% of the OSHA permissible exposure limit of 3 ppm, 8-hr TWA, and OSHA short-term exposure limit of 5 ppm. The nine areas sampled were within these limits. Engineering controls appear to reduce expected levels of formaldehyde, but no exact conclusions can be made since no samples were taken with no controls in place. Natural ventilation appears to provide the major control of exposure, with engineering controls reducing exposure in some specific cases.

REFERENCES

1. Leidel, N. A.; Busch, K. A.; and Lynch, J. R. Occupational Exposure Sampling Strategy Manual. Cincinnati, OH; U.S. Department of Health, Education, and Welfare, 1977 January. p. 95.

2. Beasley, R. K.; Hoffmann, C. E.; Rueppel, M. L.; and Worley, J. W. Sampling of Formaldehyde in Air with Coated Solid Sorbent and Determination by High Performance Liquid Chromatography. Analytical Chemistry, 52(7):89, 1980 June.

3. Industrial Ventilation - A Manual of Recommended Practice American Conference of Governmental Industrial Hygienists, committee on Industrial Ventilation. Lansing, MI, 1980. 16th Ed. p. 4-3.

APPENDX A

SAFETY RULES

SAFETY RULES

The following safety equipment is available to all RCI employees and will be expected to be used by you when necessary:

1. Face shields
2. Goggles
3. Cloth work gloves
4. Rubber work gloves
5. Rubber laboratory gloves
6. Rubber coats
7. Rubber suits
8. Boots
9. Gas mask
10. Flash lights
11. Safety helmet
12. Coveralls
13. Safety belts, harness and lines
14. Direct air respirators

1. Use of goggles or face shields:

   A. Disconnecting any line where there is a possibility of pressure build up.
   B. Handling any corrosive chemicals (acid or caustic)
   C. Grinding, chipping, or handling any material in a way that a particle might be dislodged with sufficient force to cause bodily harm.

2. Gas mask (mask must be cleaned and checked before use):

   A. When entering any tank, building, or area where there is expected to be sufficient gas vapors or dust concentration to cause respiratory difficulties (HCHO in excess of 3 ppm).

B. When removing any line or equipment where there is a possibility of discharge of material which would cause respiratory difficulties.

C. Oxygen content, HCHO content, and explosiveness must be checked before entering hazardous areas.

3. Hazardous area (tank, vessels, etc.):

   A. No one shall enter any hazardous vessel without taking the necessary safety measures as follows:

      1. Gas masks must be cleaned and checked for proper operation and equipped with new filters (inside and outside element). Oxygen content minimum (19.5%), HCHO content and explosiveness must be checked.
      2. Safety belt must be worn with line extended to safe area.
      3. No one shall stay in a hazardous area more than 30 minutes without a 15 minute break. Oxygen content, HCHO content, and explosiveness must be checked every 15 minutes.
      4. If extreme difficulty in breathing is experienced, or if a trace of chemical odor is detectd while using a gas mask, a direct air respirator must be used.
      5. Any areas to be exposed to non-explosive-proof motors, welding, or open flame must be checked with the explosive meter first before operation.
      6. An assistant must always be stationed in a safe area to render aid if necessary. He must have at his disposal a direct air respirator, gas mask, protective clothing and a fire extinguisher (Type A, B, or C). He must also have easy access to the safety line of the man in the hazardous area.

7. All vessels must be boiled out and rinsed for 24 hours before entering. The management will advise when suitable.

4. Ascending tanks, towers, etc.:

   A. Any one climbing or working above the ground where he is not completely protected by guard rails must use a safety belt or harness with a support lanyard. The lanyard must be attached at all times.

5. Hazardous chemicals (acid, caustic, ammonia, etc.):

   A. All persons handling hazardous chemicals shall use shields or goggles, gloves, hats, and coveralls.

6. HCHO (atmospheric) must be checked once per shift (maximum concentration is 3 ppm) and logged.

APPENDIX B

FORMALDEHYDE AND METHANOL SAMPLING AND ANALYSIS METHODS

Sampling of Formaldehyde in Air with Coated Solid Sorbent and Determination by High Performance Liquid Chromatography

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A method for the specific determination of formaldehyde in air is described. Formaldehyde is sampled with silica gel coated with 2,4-dinitrophenylhydrazine. The sorbent is extracted with acetonitrile, and the hydrazone is determined by reverse-phase HPLC with UV detection at 340 nm. The method was validated over the range of 2.5–93.3 µg formaldehyde (0.10–3.8 ppm for a 20-L air sample). Average recovery was 94 percent, with a relative standard deviation of 0.04.

Potential occupational exposure to formaldehyde, a major industrial chemical worldwide, has been a serious concern. The concern is based on its significant irritant effects (*1–3*) and on its potential to react with hydrochloric acid to form bis(chloromethyl) ether, a known carcinogen (*4*). The concern has intensified recently with the announcement by the Chemical Industry Institute of Toxicology (*5*) that preliminary results of a long-term inhalation study indicate formaldehyde is a carcinogen in rats.

Many methods for the determination of formaldehyde in air have been reported (*2, 6–12*), but none allows convenient, reliable, and specific measurement of personnel exposure. We now report a new solid sorbent procedure for formaldehyde which overcomes these problems. The sorbent is silica gel coated with 2,4-dinitrophenylhydrazine. Analysis of the resulting hydrazone derivative is by HPLC with UV detection, giving the desired specificity. Humidity and storage effects are reported, along with the results of validation, field testing, and comparison with the widely used chromotropic acid procedure

EXPERIMENTAL

Reagents Formaldehyde (37%), dimethyl formamide, and hydrochloric acid were Fisher Certified ACS grades Acetonitrile was Burdick & Jackson distilled-in-glass Silica gel was from Aldrich (Catalog No 21,441-8, Grade 15, 35–60 mesh)

2,4-Dinitrophenylhydrazine (2,4-DNPH) was from Matheson, Coleman, and Bell Authentic formaldehyde hydrazone derivative was prepared by a literature procedure (*13*), and recrystallized three times from ethanol mp, 164–165 °C (lit mp, 166 °C)

Certified paraformaldehyde permeation tubes were purchased from Metronics Corporation α-Polyoxymethylene (α-POM) permeation tubes were prepared from α-POM supplied to us by W M Haynes of the Environmental Analytical Sciences Center, Monsanto Research Corporation, Dayton, Ohio

Apparatus Portable sampling pumps were Models P200 and P4000 from E I du Pont de Nemours & Co, Inc

The HPLC system used was a Waters Model 6000A pump, a Rheodyne Model 70-10 injection valve with Model 70-11 loop filler port and 50-μL fixed volume loop, a Waters Model 440 UV-visible absorbance detector fitted with a 340-nm wavelength kit, and a Houston Instrument Omniscribe B-5000 recorder fitted with a Spectrum 1021A filter and amplifier A Waters C_{18}/Corasil guard column was used with a Supelco Supelcosil LC-8 (150 × 4 6 mm) analytical column

A Metronics Dynacalibrator Model 450 permeation system with high temperature option was used

A General Eastern Model 400C relative humidity/temperature monitor was used in the humidity studies

Generation of Formaldehyde Standard Permeation tubes of α-POM were prepared using 40 mg α-POM per cm of active tube length in $^1/_4$-in o d Teflon tubing (1-mm wall thickness) Both the α POM tubes and the purchased paraformaldehyde tubes were used successfully to generate a dynamic standard of formaldehyde in air, as judged by excellent correspondence of weight losses with responses obtained by the present sampling and analytical procedure The permeation chamber was held at 98 °C for α-POM and at 79 °C for paraformaldehyde Permeation rates were 443 ng/min/cm and 96 ng/min/cm, respectively

Preparation of 2,4-DNPH-Coated Silica Gel Very careful attention must be given to the details of this procedure to obtain a packing of suitable capacity and recovery For example, the mixture of 2,4-DNPH in DMF is unstable and must be used quickly DMF is used because of its superior solvent properties

Silica gel, 12 5 g, is placed in a 100-mL round bottom (RB) flask, followed by 12 5 mL of 6 N HCl DMF, 40 mL, is added to a 50-mL volumetric flask containing 5 0 g 2,4-DNPH This mixture is swirled 10–15 s, quickly diluted to the mark with additional DMF, and immediately poured through a glass wool plug in a funnel into the flask containing the silica gel and HCl The volumetric flask and glass wool are rinsed with an additional 5 mL of DMF, which is also added to the RB flask The mixture is allowed to stand for 30 min, with occasional swirling, before isolation by vacuum filtration The coated silica gel may be rinsed *sparingly* with DMF (2–3 mL) Excessive washing will result in decreased capacity for formaldehyde It is left on the filter paper with continued suction for 1–2 min and then transferred quickly to a 100-mL RB flask It is dried under vacuum at 55 °C for 1 h, with brief turning every 10 min Continuous turning, as on a rotary evaporator, was found to grind the particles too finely and result in unacceptable back pressure in subsequent air sampling Much longer drying times, as overnight, apparently completely remove residual DMF and result in decreased collection efficiency

The straw yellow-colored coated silica gel so obtained is stored in a glass bottle containing a stopper of polypropylene or other acceptable material Bakelite caps must not be used, as they will contaminate the coating The coating normally is stable for at least 1 month but should be rechecked for quality every week or so

Preparation of Sampling Tubes The collection device is a glass tube, 10 cm × 4 mm i d × $^1/_4$ in o d, containing a 300-mg front section and 75-mg back-up section of the coated silica gel The silica gel is retained at each end and the two sections are separated by small plugs of glass wool It is useful to have a small indentation in the glass tube behind the back-up section to ensure the packing is held in place during sample collection

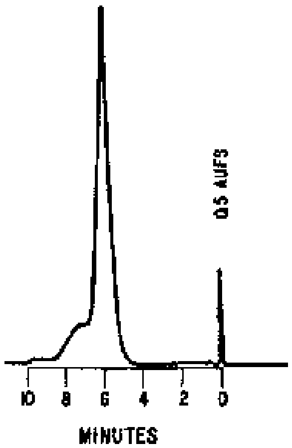

Figure 1. HPLC chromatogram for injection of 4 6 μg of formaldehyde-2,4-dinitrophenylhydrazone (equivalent to 1 08 ppm formaldehyde in air, for a 20-L air sample)

Tubes prepared as described here were found to have a pressure drop of 7 6 in H_2O at a flow rate of 115 mL/min They have a capacity of ~123 μg CH_2O (5 ppm for a 20-L air sample) before significant breakthrough occurs, regardless of humidity

Air Sampling. Sampling in the laboratory was done by connecting one end of a sampling tube to the "Stream Outlet" of the Dynacalibrator via a short length of $^1/_4$ in o d Teflon tubing and the other end to one of the Du Pont pumps Formaldehyde loadings were varied by time of collection with constant permeation and flow rates Typically, the output of the permeation device was set for ~1 0 ppm and was "sampled" at 100–200 mL/min For studies where a full 20-L or more air sample was desired but not obtained by this sampling procedure, the make-up air was obtained from additional "sampling" of zero air supplied by the Dynacalibrator

For the humidity studies, the additional air was humidified by bubbling through a saturated solution of potassium sulfate (96–99% relative humidity) in an apparatus that was all glass except for the probe of the humidity monitoring device

Field samples in production facilities were obtained using the Du Pont pumps A typical sampling rate was 110 mL/min For field experiments with spiked tubes, the spike was applied to the tube in the laboratory using the procedure described above

Analysis. The front section of the collection tube, including the front glass wool plug, is transferred to a 1-dram vial containing 2 0 mL acetonitrile The back-up section and the glass wool plug that separates the two sections are treated similarly The vials are stoppered with polypropylene caps (no Bakelite) and allowed to stand overnight

For analysis, ~0 2 mL of the desorbing solution is injected into the loop filler port to provide flushing and loading of the 50-μL injection volume The system also is flushed with CH_3CN between injections Mobile phase for the analysis is 65/35 (v/v) water/acetonitrile, pumped at 2 0 mL/min Typical chromatograms are shown in Figures 1–3

Quantitation in this work was done by peak height using a calibration curve generated from a series of standards containing 10–400 μg/mL authentic formaldehyde 2,4 dinitrophenylhydrazone in acetonitrile (corresponding to ~0 1–4 6 ppm CH_2O in air for a 20-L sample)

RESULTS AND DISCUSSION

Sampling for personnel exposure by trapping the substance of interest on a solid sorbent has become a fairly routine practice (*14*) The material is desorbed from the sorbent, either thermally or with solvent, and subsequently determined
90 by various techniques, often specifically Solid sorbent sampling for personnel exposure is much preferable to liquid absorbing techniques because of potential risks to the worker

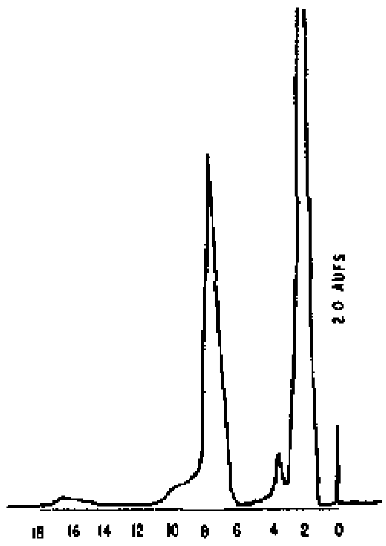

Figure 2. HPLC chromatogram for injection of sample resulting from collection of 122 μg of formaldehyde (4.96 ppm for a 20-L sample) on a 2,4-DNPH coated silica gel tube as described in the Experimental section.

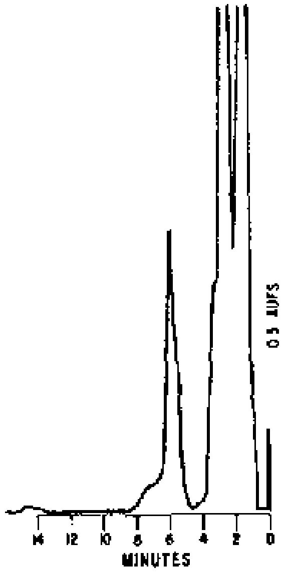

Figure 3. HPLC chromatogram for a field sample at a location where formaldehyde is used as a raw material. The sample was determined to represent 0.85 ppm formaldehyde in air.

posed by glass impingers containing various liquids.

Unfortunately, the solid sorbent technique is often difficult to do with highly reactive molecules. The material may not maintain its chemical integrity during sampling or subsequent storage prior to analysis. It may oxidize, hydrolyze, polymerize, or undergo other transformations. Wood and Anderson (*7–10*) screened many solid sorbents for sampling formaldehyde and found none entirely suitable for formaldehyde retention at high humidity levels. Finally, alumina was chosen, but it could be used for only a 30-min sampling period and had to be desorbed immediately to prevent poor recovery.

A logical approach for formaldehyde and other reactive molecules then is to coat the solid sorbent with some material which will either moderate the reactivity or else take advantage of it and direct it toward stable products which can be readily desorbed and analyzed, and which are as specifically indicative of the original substance of interest as possible. This approach may also help with the problem of low sorbent capacity that is observed often with small molecules.

Hurley and Ketcham (*15*) applied this approach to acrolein, which was sampled with charcoal treated with hydroquinone. Our method (*16*) for chloroacetyl chloride in air is related. The acid chloride is trapped on silica gel and determined by ion chromatography as its hydrolysis products, monochloroacetate and chloride. Here the "derivatizing" agent is water, which has a high affinity for silica gel.

Kim, Geraci, and Kupel (*11*) recently reported a solid sorbent procedure for formaldehyde which utilizes this concept. Formaldehyde is sampled on charcoal impregnated with an oxidizing agent, proprietary to Barneby-Cheney Co. The reactive formaldehyde is oxidized to the more stable formate species, which is subsequently desorbed and determined by ion chromatography. This is a significant improvement over previous methods, but it is not completely specific for formaldehyde, and it may not be readily extrapolatable to other aldehydes and certainly not to ketones.

Use of the coated solid sorbent approach for formaldehyde works well in the present case. 2,4-Dinitrophenylhydrazine gives a stable derivative which may be determined with good sensitivity by HPLC.

Sampling. The key to the present work is the successful preparation of 2,4-DNPH-coated sorbent of suitable capacity, collection efficiency, and derivative recovery. Various sorbents, including alumina, molecular sieves, and Ambersorb XE-347, were investigated before selecting silica gel. DMF was selected as the best solvent for 2,4-DNPH, although significant problems with instability of the 2,4-DNPH–DMF mixture had to be overcome. Approximately 20 experiments were done to define the best sequence and timing of operations. Several key points were identified. One of these was the necessity of having HCl in the preparation, possibly either to catalyze the reaction of 2,4-DNPH with CH_2O or to activate the silica gel surface. Coated solid sorbent prepared without HCl gave results 11% lower than those where HCl was used. The relative decrease was constant over a 20-fold range of formaldehyde loading, indicating it was due to decreased collection efficiency and not to decreased capacity. More striking was the effect of order of addition of reagents. Sorbent prepared in which the 2,4 DNPH was dissolved first in HCl, to preform the hydrochloride salt, followed by DMF, had a 40% decrease in collection efficiency. This result is not well understood but may have to do with wetting of the silica gel. The procedure as defined in the Experimental section has been found to reproducibly give coated silica gel with a good collection efficiency, capacity for ~5 ppm formaldehyde (for a 20-L air sample), and derivative recovery greater than 90%. However, every batch of coated silica gel should be checked in the laboratory to ensure quality before its use for field sampling.

The choice of acetonitrile for desorbing solvent gives good recovery of the formaldehyde derivative and is highly compatible with the mobile phase in the subsequent HPLC analysis.

Analysis. Several reports (*6, 17, 18*) have appeared previously on high performance liquid chromatography of 2,4-dinitrophenylhydrazones, including one (*6*) specifically for determining aldehydes in air using impingers containing 2,4-DNPH. Detection was by UV at 254, 336, or 340 nm.

In our hands, the chromatography was straightforward. At the levels of interest, we encountered significant background problems at 254 nm. These were not present at 340 nm.

A typical chromatogram for authentic formaldehyde 2,4-dinitrophenylhydrazone is shown in Figure 1. The nature of the small shoulder on the back side of the hydrazone is not known, but it was reproducible and also was observed in samples from the trapping of laboratory-generated standard formaldehyde or field samples with the 2,4-DNPH-coated silica gel tubes (Figures 2 and 3). That it is observed with

Table I Results for Validation of Formaldehyde Method

CH_2O air concn , ppm[a]	CH_2O found, ppm[b]	% recovery	RSD[c]
0 09	0 08	89	0 0001
0 44	0 42	95	0 042
1 03	1 00	97	0 034
2 04	1 89	93	0 049
3 78	3 61	96	0 040

[a] Based on a 20-L air sample. Amount based on weight loss of permeation tube and time of collection at constant rate [b] Average of six samples Measurements were tested for outliers by Grubbs' test (*19, 20*) at the 99% confidence level [c] Pooling of the individual RSDs gives the result of 0 037 with a χ^2 value from Bartlett's test (*19, 21*) of 49 50 Omitting the RSD at the 0 09-ppm level results in a pooled RSD of 0 041, with χ^2 of 0 62 (critical values for χ^2 at the 0 01 level are 13 28 for four degrees of freedom and 11 34 for three degrees of freedom)

authentic hydrazone indicates it is not related to the 2,4-DNPH-DMF instability problem Its relative retention changes depending on the particular HPLC column used A Waters Associates μ-Bondapak C_{18} column was found to give a single sharp peak with no shoulder Use of a Zorbax ODS column (Du Pont) resulted in a small shoulder on the front side of the main peak

A small background peak, equivalent to ~0 08 ppm CH_2O for a 20-L air sample, was routinely present in "blank" samples prepared in the laboratory One source of contamination that was observed and should be avoided is Bakelite bottle caps Bakelite, of course, is a polymer prepared from formaldehyde and phenol Apparently enough free formaldehyde is available to cause a low level background

Validation The method was laboratory validated by generating six samples at each of five levels, equivalent to 0 1–3 8 ppm formaldehyde for a 20-L air sample The results are summarized in Table I Average recovery was 94% The pooled coefficient of variation, or relative standard deviation, was 0 04 Precision at the lowest level is probably artificially good due to the inadequacy of the peak height measurement at this level A linear regression of formaldehyde expected vs found showed excellent correlation, with a slope of 0 95 and an intercept of −0 01 ppm

The back-up sections of all validation samples were analyzed also No breakthrough was observed

Humidity Studies. For uncoated solid sorbents, where the collection is clearly by an adsorption process, increased humidity generally results in an increase in breakthrough For formaldehyde particularly (*7–10*), this was noted to be a significant problem Possible humidity effects in the present case were studied by examining both breakthrough and recovery of formaldehyde spikes on 2,4-DNPH-coated silica gel tubes that were used to "sample" 20 L of air at 96–99% relative humidity

The spike in all cases was equivalent to 4 ppm formaldehyde and was applied by the permeation device either before any air was sampled or after 5 of the 20 L had been sampled The latter case allowed the sorbent to be somewhat preconditioned to any potential effects of the high humidity

No breakthrough into back-up sections was observed, and recoveries of formaldehyde or the derivative, either immediately after sampling or after five days' storage, were within the statistical limits of the validation results, with no apparent bias

Storage Effects. Often it is not practical to analyze or even to desorb a sample for several days, particularly if the sample is being shipped off-site for analysis In some cases this results in significant sample loss or, particularly in the case of volatile compounds, significant migration of sample to the back-up section, resulting in a false indication of breakthrough

In the present case, storage studies indicated that samples should be desorbed within 1–2 days for maximum recoveries Losses up to 30% can occur after 5 days The resulting desorbed mixtures are stable for some time Recovery of formaldehyde was unchanged for up to 20 days for refrigerated desorbed solution from which the glass wool and silica gel were removed after one day and for at least nine days if the glass wool and silica gel were not removed

Field Tests. The performance of this method was evaluated in several tests at three industrial locations where formaldehyde is used as a raw material in two widely different processes and where a great diversity of other chemical processes are in operation nearby Approximately 75 samples were taken No sampling or analytical problems were observed No breakthrough into a back-up section was found The largest loading was 108 μg formaldehyde, obtained over a period of 3 0 h at 113 mL/min (ambient temperature, ~32 °C, relative humidity, 53%)

Some additional field results are discussed in the next section

Comparison to Chromotropic Acid Procedure The most widely used procedure for formaldehyde in air is collection of sample in an impinger of water and subsequent spectrophotometric determination using the chromotropic acid procedure (*12*) In addition to the usual disadvantages of impinging methods, the chromotropic acid procedure has long been recognized to be subject to many interferences We compared the new coated solid sorbent procedure with the chromotropic acid method and found that the new procedure gives higher results both in the laboratory and in the field Furthermore, the solid sorbent result appears to be the "correct" answer

In the laboratory, water-containing impingers were used to collect standard formaldehyde vapor from the permeation device Subsequent determination was done with chromotropic acid, with calibration based on formalin solution whose concentration had been determined by titration with iodine These results often were 15–30% lower than those from comparable samples using the 2,4-DNPH-coated silica gel tubes, with calibration based on authentic hydrazone derivative The hydrazone results agreed exactly with calculated results based on weight loss from the permeation tube As an additional cross-check, the formalin solution also was determined using 2,4-DNPH and HPLC This result and the iodine titration result were identical

The lower results with the impingers are not due to poor collection efficiency or to sample stability, since formaldehyde levels did not decrease when up to 55 L of air were passed through the system over 3 h at temperatures up to 49 °C

The discrepancy between the two methods was checked further in the field tests Results from the chromotropic acid procedure were 27–28% lower than those from the coated silica sorbent method

The results from one field study are shown in Table II Four solid sorbent tubes and four impinger assemblies were set at the same sampling location The various devices were within a few inches of each other but the sampling inlets were not in intimate contact. The mean of the solid sorbent results was 2 2 ppm, with a standard deviation of 0 3 ppm The mean of the impinger results was 1 6 ppm, with a standard deviation of 0 2 ppm An unpaired T test showed that these results were statistically different at the 95% confidence level

The results of another field test using both spiked and nonspiked solid sorbent tubes and impingers are shown in

Table II Results of Parallel Field Tests Using 2,4-DNPH-Coated Silica Gel[a] and Water Impingers[b]

replicate no	formaldehyde found, ppm	
	from coated gel	from impinger
1	2 4	1 7
2	1 9	1 9
3	1 9	1 4
4	2 4	1 4
	$\overline{X}$ = 2 2, σ = 0 3	$\overline{X}$ = 1 6, σ = 0 2

[a] Samples analyzed by the HPLC method described in the Experimental section [b] Samples analyzed by the chromotropic acid procedure (*12*)

Table III Results of Field Tests Using Both Spiked and Unspiked Collection Devices

sample type	no of samples	CH_2O spiked, ppm	total CH_2O found, ppm	ambient CH_2O concn (total minus spiked) ppm
coated silica gel	3	0 88	1 78	0 90
coated silica gel	3	0 0	0 87	0 87
impinger	3	0 75	1 40	0 65
impinger	3	0 0	0 66	0 66

Table III In this test, the spiking amount was fortuitously almost identical to the ambient formaldehyde concentration observed Good spike recovery was observed The impinger results were 28% lower than in the solid sorbent results

After completion of this work a similar method, using GC analysis and XAD-2 resin coated with 2,4-dinitrophenylhydrazine, was reported (22)

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LITERATURE CITED

(1) L G Wayne and R J Bryan Irritant Effects of Industrial Chemicals: Formaldehyde DHEW (NIOSH) Publication No 77-117 Cincinnati, Ohio, 1976

(2) J R Finkles, Criteria Document Recommendations for an Occupational Exposure Standard for Formaldehyde DHEW (NIOSH) Publication No 77-126 Cincinnati Ohio, 1976

(3) L E Kane and Y Alarie, *Am Ind Hyg Assoc J* 38 509 (1977)

(4) C C Yao and G C Miller, Research Study on Bis(Chloromethyl) Ether Formation and Detection in Selected Work Environments DHEW (NIOSH) Publication No 79-116 Cincinnati, Ohio, 1979

(5) M Heylin Ed, *Chem Eng News* Oct 22 1979, p 7

(6) K Kuwata M Uebori and Y Yamasaki, *J Chromatogr Sci*, 17 264 (1979)

(7) G O Wood and R G Anderson Air Sampling of Formaldehyde with a Solid Sorbent Tube presented at the American Industrial Hygiene Conference Minneapolis Minn, 1975

(8) G, O Wood and R G Anderson Development of Air Monitoring Techniques Using Solid Sorbents, Los Alamos Scientific Laboratory Report LA-6216-PR, 1976 Available from NTIS

(9) E E Campbell G O Wood and R G Anderson Development of Air Sampling Techniques Los Alamos Scientific Laboratory Report LA 5634-PR, 1974 Available from NTIS

(10) E E Campbell G O Wood and R G Anderson Development of Air Sampling Techniques, Los Alamos Scientific Laboratory Report LA-5973-PR, 1975 Available from NTIS

(11) W S Kim, C L Geraci and R E Kupel Ion Chromatographic Determination of Some Organic Acids and Formaldehyde in the Industrial Atmosphere, presented at the Second National Symposium on Ion Chromatographic Analysis of Environmental Pollutants Raleigh N C 1978

(12) J V Crable and D G Taylor NIOSH Manual of Analytical Methods" DHEW (NIOSH) Publication No 75-126 Cincinnati Ohio 1974

(13) S M McElvain, *The Characterization of Organic Compounds* Macmillan New York 1953 p 205

(14) R G Melcher R R Langner and R O Kagel, *Am Ind Hyg Assoc J* 39 349 (1978)

(15) G. F Hurley and N H Ketcham, *Am Ind Hyg Assoc J* 39 615 (1978)

(16) P R McCullough and J W Worley *Anal Chem* 51 1120 (1979)

(17) C T Mansfield, B T Hodge R B Hege Jr and W C Hamlin *J Chromatogr Sci* 15 301 (1977)

(18) S Selim, *J Chromatogr* 136 271 (1977)

(19) D G Taylor R E Kupel and J M Bryant Documentation of the NIOSH Validation Tests DHEW (NIOSH) Publication No 77-185 Cincinnati Ohio, 1977

(20) F E Grubbs and G Beck *Technometrics* 14 847 (1972)

(21) R Bethea, B Duran and T Boullion Statistical Methods for Engineers and Scientists, Marcel Dekker New York 1975 pp 247-251

(22) G Andersson and K Andersson *Chemosphere* 823 (1979)

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Formaldehyde Sampling Procedures

1) The sampling tubes should be placed in a vertical position during sampling to minimize possible channeling through the tubes.

2) The tubes labelled "Blank" and "Spiked Blank" should be placed, with end caps on, in the area sampling is taking place. These tubes are for quality control purposes.

3) Two tubes, one "Spiked" and one unspiked, should be used to sample the area simultaneously under the same conditions.

4) The unspiked tube sampled along side the "spiked" tube in Step #3 should be properly identified.

5) A "Blank" tube and "Spike" tube as in Steps #2 and #3 should be used each sampling day in the manner previously described.

6) Please keep the sampling tubes refrigerated when not in use to enhance the stability of the packing.

7) The packing material in the sampling tubes is stable for two weeks only Therefore, prompt sampling and analysis is important.

Methyl Alcohol

Analyte:	Methyl Alcohol	Method No.	S59
Matrix	Air	Range	140-540 mg/cu m
OSHA Standard	200 ppm (260 mg/cu m)	Precision ($\overline{CV}_T$).	0 070
Procedure	Adsorption on silica gel, desorption with water, GC	Validation Date	1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a silica gel tube to trap the organic vapors present.

1.2 The silica gel in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with water.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1 4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2 Range and Sensitivity

2.1 This method was validated over the range of 140-540 mg/cu m at an atmospheric temperature and pressure of 25 C and 745 mm Hg, using a nominal 5-liter sample. Under the conditions of sample size (5 liters) the probable range of this method is 35-900 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 4-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2 2 The upper limit of the range of the method is dependent on the adsorptive capacity of the silica gel tube This capacity varies with the concentration of the analyte and other substances in the air. The first section of the silica gel tube was found to hold 5.6 mg of the analyte when a test atmosphere of 540 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 52 minutes. Breakthrough occurred at this time,

i.e., the concentration of the analyte in the effluent was 5% of that in the influent. (The silica gel tube consists of two sections of silica gel separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 140 to 540 mg/cu m was 0.063. This value corresponds to a standard deviation of 16.5 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 8.9% lower than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the silica gel tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate. (Reference 11.2)

6.2 Silica gel tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam. The absorbing section contains 100 mg of silica gel, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

6.5 An electronic integrator or some other suitable method for determining peak size areas.

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Distilled water

7.2 Methyl Alcohol (reagent grade).

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps Each personal pump must be calibrated with a representative silica gel tube in the line This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of silica gel is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The silica gel tube should be placed in a vertical direction during sampling to minimize channeling through the silica gel.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the silica gel tube.

8 3.5 A maximum sample size of 5 liters is recommended. Sample at a flow of 0.20 liters per minute or less The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded

8.3.7 The silica gel tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the silica gel tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each silica gel tube is scored with a file in front of the first section of silica gel and broken open. The glass wool is removed and discarded. The silica gel in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of distilled water is pipetted into each sample container. Desorption should be done for 4 hours. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the water is added to minimize evaporation.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).
6. 80 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of silica gel to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process.

8.5.2 Procedure for determining desorption efficiency. Silica gel equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This silica gel must be the same type as that used in obtaining the samples and can be obtained from unused silica gel tubes. A known amount of the analyte is injected directly into the silica gel with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 5-liter sample at the selected level.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the silica gel. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the silica gel. Plot the desorption efficiency versus the weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9 Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area.

Note: Standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10 Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where·

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of analyte in the air sampled can be expressed in mg per cu m, which is numerically equal to µg per liter of air

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)