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DETAILED INDUSTRIAL HYGIENE SURVEY
FORMALDEHYDE PRODUCTION

E. I. DuPont DeNemours & Co.
Chemicals and Pigment Department
Grasselli Plant
Linden, New Jersey 07036

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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 detection 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, administrative, or work practice controls. Normally indicates an exposure equal to or 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

GLOSSARY OF TERMS (continued)

double mechanical seal	a multiple seal arrangement that uses two single mechanical seals oriented back-to-back with a fluid filled space between them
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 a 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	contact 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 or worker activity that requires an extended period of time to complete, usually a full work shift
MeOH	symbol used for methanol
min	minute

GLOSSARY OF TERMS (continued)

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 concentration of HCHO which should not be exceeded even instantaneously, which is 5 ppm
OSHA HCHO TWA PEL	the time-weighted average concentration of formaldehyde which should not be exceeded in an 8-hour work shift of a 40-hour work week - limit is 3 ppm
OSHA MeOH TWA PEL	the time-weighted average amount of methanol which should not be exceeded in an 8-hour work shift of a 40-hour work week - 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

GLOSSARY OF TERMS (continued)

PIHS	preliminary industrial hygiene survey; an in-plant survey conducted in order to gain approximate information on worker exposure, work practices, engineering controls, process flow, and the plant safety and health program
ppe	personal protective equipment; equipment worn by a worker, as a respirator, used to prevent potential worker over-exposure 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
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 short-term concentration limit set for contaminant exposure

GLOSSARY OF TERMS (continued)

TWA	time-weighted average, the average concentration of a sample or a set of consecutive samples, weighted by the time sampled
walk through survey	a preliminary industrial hygiene survey

1. INTRODUCTION

This detailed industrial hygiene survey report describes one five-day and one three-day survey conducted at the DuPont formaldehyde production unit in Linden, New Jersey. This plant uses a silver oxide catalyst to convert methanol to formaldehyde at a rated capacity of 160 million pounds of formaldehyde per year. The plant was selected for detailed study based on its good engineering controls and ability to control worker exposure to formaldehyde and methanol.

1.1 PLANT PERSONNEL CONTACTED

The plant surveys described in this report were carried out by personnel from Monsanto Research Corporation (MRC) and Geomet Technologies, Inc. (GTI) on October 25-29, 1982 and June 13-16, 1983 The October 1982 survey was conducted by Glen Barrett, CIH (GTI) and David Dunn, Harlan Toy, and Leroy Holmes (MRC). The June 1983 survey was conducted by Glen Barrett, CIH (GTI) and David Dunn and Arthur Wright (MRC). Personnel contacted during the visits included Harry W. McDowell, Safety, Health, and Environmental Manager for the plant; Robert Mansfeld, plant laboratory supervisor; and John Gurley, senior supervisor for the production unit The environments of several of the workers under Mr. Gurley's supervision were sampled for formaldehyde and methanol during the survey. Side-by-side sampling was conducted by DuPont personnel when MRC personnel took most of their samples.

1.2 SUMMARY OF ACTIVITY

The team met with plant personnel on October 25, 1982 and on June 13, 1983 to discuss the objectives of the survey and the activities to be done to pursue these objectives. Coordination of sampling activities was also discussed. A short walk-through of the production unit was made to acquaint the survey team with the formaldehyde production area. During the first visit the base of operations was set up in a corner of the control room. During the second visit the base of operations was set up in a control laboratory remote to the formaldehyde production area to minimize the chances of sample contamination. All equipment was checked, including pump calibration.

During the first visit, industrial hygiene sampling began on the day shift, Monday, October 25, and continued through the day shift, Friday, October 29. A total of nine worker shifts (5 day shifts;

4 night shifts) were sampled. No sampling was conducted during the third shift due to logistics and similarity of operation on all shifts

Analyses of the MRC quality assurance samples for methanol indicated that the results of the methanol analyses were reliable. However, analyses on the formaldehyde quality assurance samples taken during the first visit showed that the resulting data were not reliable, possibly having been seriously contaminated. It was decided that these data would not be used for the evaluation of exposures at the Linden, NJ plant.

Since the formaldehyde data from the first visit had to be discarded, a second visit was made to do formaldehyde sampling in June 1983 During this visit the sampling team met with DuPont plant personnel on Monday, June 13. Formaldehyde sampling was performed during the day and night shifts on Tuesday and Wednesday, June 14 and 15, and on the day shift on June 16.

Table 1 shows the total number and types of samples collected during the surveys Personal exposure samples for formaldehyde and methanol were taken by sampling individuals who worked in the plant area. Long-term (over one hour) personal samples were taken to evaluate the workers' general exposure. Short-term (generally less than one hour) samples were taken on personnel to evaluate specific operations the worker conducted on a regular basis. Area samples were taken to determine the potential exposure of a worker in an area and to generally evaluate formaldehyde and methanol concentration in the production and storage areas. Source samples were taken to evaluate the contribution of specific equipment to the overall area concentrations and to evaluate the exposure control achieved by this equipment.

TABLE 1. SAMPLES COLLECTED DURING IH SURVEY AT THE DUPONT FORMALDEHYDE PLANT IN LINDEN, NJ

	Formaldehyde		
Type	Long-term	Short-term	Methanol
Personal	18	8	15
Area	23	7	21
Source	-	4	2
Total	41	19	38

Note: Does not include spike and blank tubes used for MRC Quality Assurance.

Observations of operator work practices were also made during the surveys. In addition, control and process equipment were noted and discussed with Mr. Gurley to aid in evaluating this equipment and comparing it to equipment at other plants.

Closing conferences were held with Mr. McDowell to discuss future use of the data collected and to thank the plant personnel for their cooperation

2. BACKGROUND

2.1 GENERAL

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).

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

The objectives of the IH/CTA study are to:

a evaluate the state-of-the-art control technology in the formaldehyde production industry,

b evaluate the effectiveness of industrial hygiene control programs to control these potential hazards,

c. identify potential hazards to workers,

d. evaluate these potential hazards for the effects on workers,

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

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

g. 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 was 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.

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 PLANT

The DuPont Grasselli plant is located in a heavily industrialized section of Union County in Linden, New Jersey. The silver catalyst formaldehyde production operation, which began in 1971, has a rated capacity of 160 million pounds per year on a 37 percent solution basis (approximately 59 million pounds of formaldehyde produced per year). Aqueous formaldehyde is shipped from the plant by truck or rail.

The formaldehyde production unit is a tri-level, open-air structure. A plant site plan (Figure 1) shows the relationship of the formaldehyde production unit to other facilities in the plant and to the plant offices. Open air construction provides for natural ventilation control of air contaminants through dilution. Two control rooms monitor the production process, one housing the chief operator who also has responsibility for a second unrelated unit, and a second room which is used as a blending and process sample analysis laboratory.

The plant operates 7 days/week, using three shifts of unionized workers per day, with a fourth shift rotated in each week. The production unit employs a total of nine persons, with an operator and chief operator on each shift and a production supervisor onsite during the day shift.

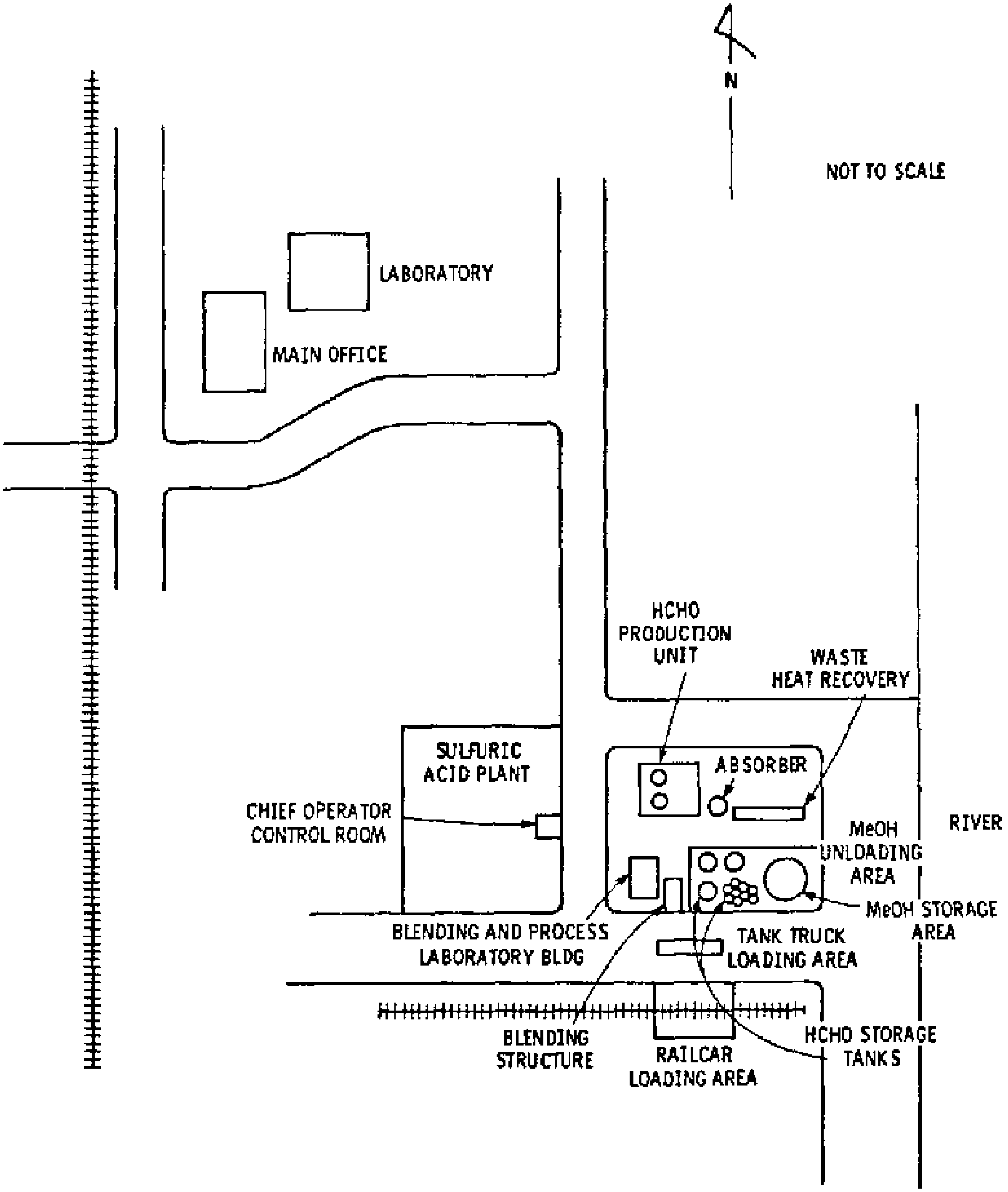

Figure 1. DuPont Grasselli Plant.

4. PROCESS DESCRIPTION

Formaldehyde is manufactured by a combination oxidation-dehydrogenation process using silver as a catalyst. The process schematic is shown in Figure 2.

Methanol is unloaded from a tank truck to a large bulk storage tank and is then pumped to the methanol vaporizer. Air is drawn through a pair of water scrubbers, preheated, and then combined with the vaporized methanol. The methanol-air mixture is fed to the converter system. Waste heat from the reaction is recovered for use by a heat exchanger system. Hot formaldehyde gas passes through a second heat exchanger and the cooled gas enters the base of a single atmospheric absorber column. Liquid effluent from the absorber, containing up to 50 percent formaldehyde, is stored in tanks. The aqueous solution also contains some methanol and formic acid. Gas emitted from the top of the absorption column, containing hydrogen, nitrogen, and traces of formaldehyde and methanol, is burned in a separate waste heat recovery boiler and the heating value recovered for use in the vaporizer. The burner is designed for 99 percent combustion efficiency. The effluent gas from the heat recovery system consists of nitrogen, carbon dioxide, and water

The product storage tanks are heated by internal steam coils to maintain the temperature which prevents paraformaldehyde formation. The formaldehyde solution is passed through an ion exchange column to remove formic acid and blended in-line to produce the desired solution for shipment. The blended products are loaded into tank trucks and rail tank cars for shipment.

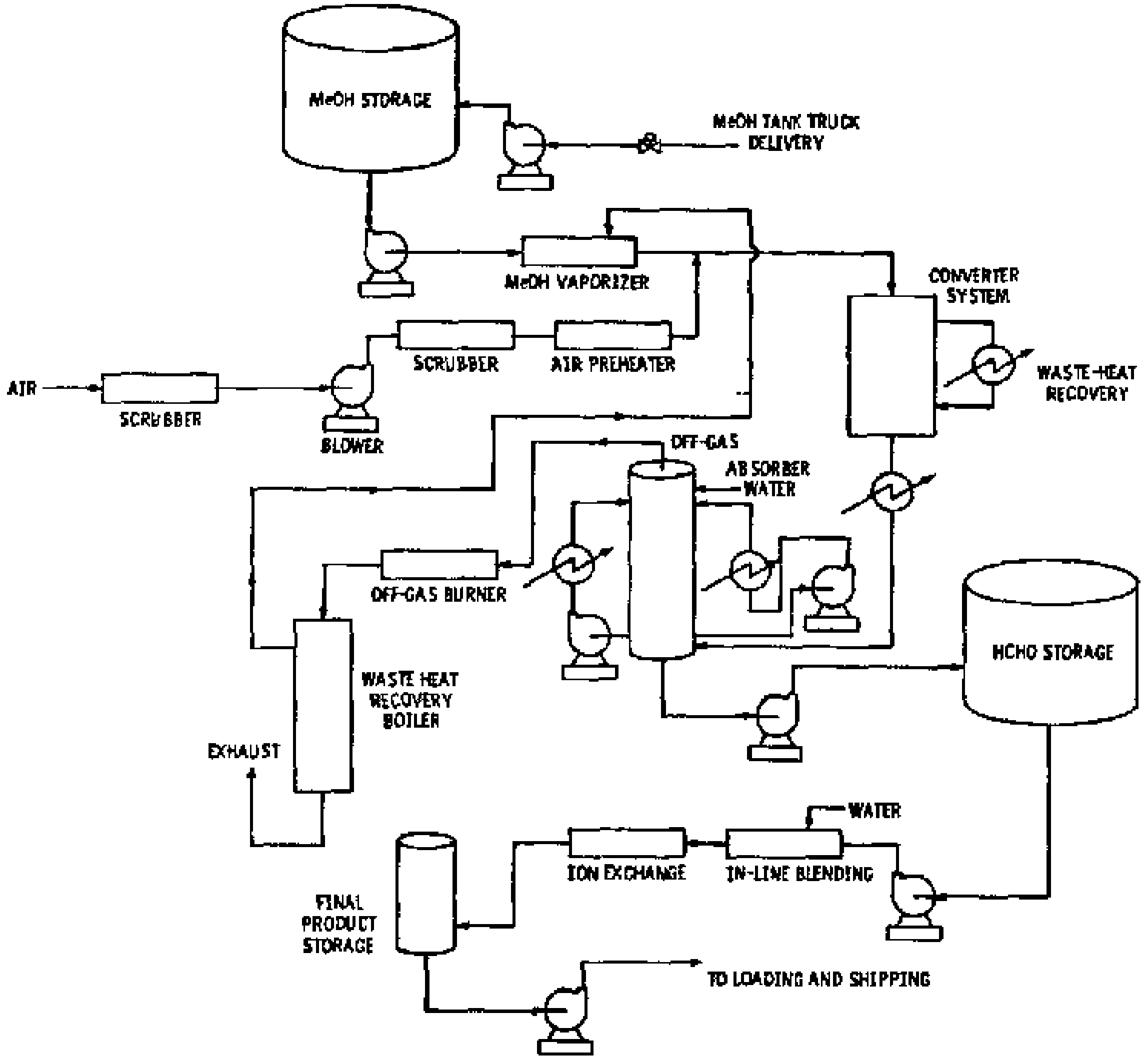

Figure 2. DuPont process schematic.

5. DESCRIPTION OF PROGRAMS

5.1 INDUSTRIAL HYGIENE

The environmental coordinator at the plant is responsible for safety, industrial hygiene, and environmental concerns. In addition to the corporate industrial hygiene group and external consulting groups, which may be used as resources, the laboratory supervisor and analysts carry out monitoring as recommended by the coordinator.

An occupational safety and health committee, consisting of supervisors and health personnel, serves for review, coordination, and program development functions. Information is reviewed and passed along to the site employees Supervisors must document that such information has been reviewed by them.

The independent union which represents the employees has no formal safety and health committee, but maintains an active interest in safety and health questions. For example, recent information on formaldehyde provided by the occupational safety and health committee was reviewed with the union.

Contingency plans for emergencies are well-defined. The nearest fire station is within several blocks, and the plant is a member of the Linden Industrial Mutual Aid Council (LIMAC) which provides for mobilization of private sector assistance in the case of fire, explosion, or other emergencies. Fire drills, which include simulation of release of toxic air contaminants, are conducted during all shifts, approximately ten times per year. Five alarm boxes are located throughout the plant complex. If a worker is injured, workers are instructed to pull a fire alarm box to notify the plant and the Linden Fire Department for assistance. Workers are trained in first aid and cardio-pulmonary resuscitation. The workers are also equipped with beepers that can be sounded by dialing an emergency number when they require assistance for an injured worker.

Safety precautions have been and continue to be integrated into the operating procedures covering each phase of operation in the plant.

Formal "lockout" procedures (isolation of personnel from danger) are used for any operation which involves "breaking" a line or using a "fire" (welding, torching, etc.).

Safety equipment (showers, eyewashes, protective clothing, self-contained breathing apparatus, fire extinguishers and blankets, and first aid kits) are located at numerous points in the plant, and are well marked Nine emergency eyewash and shower stations are located in the formaldehyde production area; including the rail and truck formaldehyde loading areas, the control building, the process structure, and the blending area. These stations are checked for proper operation on a daily basis. Each station is clearly marked by a green light. Each station is also protected from freezing water lines by insulation and automatic drains which eliminate standing water in exposed pipes.

5.2 OCCUPATIONAL SAFETY AND HEALTH (OSH) TRAINING

A formal employee training program is required for new employees. OSH training is incorporated in the on-the-job training provided by the supervisors and operators for new employees or employees assuming new duties. Safety retraining is scheduled every two years and includes fire protection and first aid.

Spill control procedures are provided for each chemical found in the plant. Training in these include use of the appropriate and specified personal protective equipment and handling procedures.

Job-cycle checks are performed every year. In these, elements of a specific aspect of the job are reviewed with the employee (e.g., tank car loading). The formaldehyde operator's job includes about 20 separate job cycles to be reviewed.

Use of respirators is an element of the training program. If operators' duties may require use of negative-pressure respirators, they are retrained once a year. The plant has modified the written corporate respiratory protection program to plant specifications.

5.3 PERSONAL PROTECTIVE EQUIPMENT (PPE)

Training in use of respirators is an integral part of the overall training program. The safety department is responsible for cleaning and maintenance of the respirators. All full-face respirator users are fit-tested (qualitative) once a year.

Specific PPE is required as follows:

All formaldehyde operations

Hard hats and side-shield safety glasses

Startup operations

Full-face respirators
Rubber gloves

Loading operations (while on the rack or vehicle)

Rubber gloves
Full-face acid gas cartridge respirator

Maintenance - major leak repair

Self-contained breathing apparatus or air-supplied respirator
Rubber gloves

Changing reactor catalyst

Rubber gloves

Formaldehyde storage tank cleanout

Complete coveralls
Respiratory protection if oxygen or formaldehyde sampling tests indicate a need

Formaldehyde sample collection

Full-face acid gas cartridge respirator
Rubber gloves

Methanol analysis

Rubber gloves

5 4 MEDICAL PROGRAM

An occupational physician is available at the plant site four afternoons per week. A full-time registered nurse is employed on-site and is on call. A fully equipped first aid facility is used for nonserious injuries Hospitals in Elizabeth, NJ, are used for major injuries. Injured workers are transported to the plant hospital in a plant-owned emergency van.

No compensation claims or work-related illness or dermatitis have been reported from the formaldehyde unit.

Pre-employment and periodic physical examinations are given. Periodic exams include completion of a health history questionnaire, examination by a physician, posterior-anterior chest X-ray, pulmonary function tests, audiometric test, urinalysis, white blood count and hemoglobin or hematocrit, complete blood tests, and an EKG.

6. WORK PRACTICES

6.1 GENERAL PROCEDURES

6 1 1 Supervisors

An overall senior supervisor manages the operations for both the sulfuric acid and formaldehyde units during the day shift. This worker, who spends very little time in the units, is not usually directly exposed to formaldehyde gas. His office, where he spends a majority of his time while at the unit, is in a building across a plant road from the formaldehyde unit and next to the formaldehyde and sulfuric acid units control building.

The production supervisor specifically supervises the formaldehyde unit operation during the day shift. His office is in the same building as the overall supervisor of the sulfuric acid and formaldehyde units. The production supervisor works in the formaldehyde unit when necessary, to ensure smooth operations. As a result, he is potentially exposed to formaldehyde gas.

6 1.2 Chief Operators

One chief operator is assigned per shift to operate the sulfuric acid and formaldehyde unit controls from within the central control building across the street from the formaldehyde unit, and next to the sulfuric acid unit. Chief operators are licensed boiler operators and spend the majority of their time in the control building They do check and blow boilers down once or more per shift, which requires them to enter the formaldehyde unit area where there is a potential for additional exposure.

6.1.3 Formaldehyde Unit Operators

One unit operator per shift is assigned to the formaldehyde production unit. Duties include blending the formaldehyde solution for shipment using the automatic blending controls, loading tank trucks and rail cars, sampling the production process, and analysis of formaldehyde and methanol samples. He is also responsible for inspecting the process to check for malfunctions or leaks and for correcting and clearing up these problems. The operator spends approximately 50 percent of his shift in a blending control/laboratory building adjacent to the truck loading area and blending structure.

6 1.4 Maintenance Workers

Maintenance of the formaldehyde and sulfuric acid units is provided by five service operators working over three shifts and 8-10 maintenance personnel, plus a supervisor, who work during the day shift. Maintenance personnel provide maintenance for the entire plant complex. They are involved with start-up operations, catalyst change, and tank entry, as well as normal plant maintenance. It is estimated that they spend no more than 20 percent of their time at the formaldehyde unit.

The service operators are involved in miscellaneous service work and clean-up for both the sulfuric acid and formaldehyde units. They spend most of their time on duties within the sulfuric acid unit.

6.2 METHANOL UNLOADING

No DuPont employee is directly involved with the delivery or unloading of methanol. Methanol is delivered to the plant by an outside contractor, whose driver performs all unloading activities. The truck driver positions the tank truck and hooks up the flexible unloading line to the bottom of the truck. The driver takes a capped methanol sample, which was collected at the facility distributing methanol, to the unit operator for analysis. After the methanol analysis is approved, the driver returns and initiates unloading. When unloading is complete, the truck driver disconnects the line and leaves. Several tank trucks are unloaded per day

6.3 METHANOL SAMPLE ANALYSIS

The formaldehyde unit operator receives the methanol sample in the unit building in a closed glass jar from the truck driver. The operator then pours approximately 200 mL of the sample into a graduated cylinder on the lab counter to the right of the laboratory hood. A hygrometer is inserted into the graduated cylinder, and the temperature of the sample solution is determined by inserting a thermometer into it. The specific gravity of the sample is then determined.

The sample is then poured back from the graduated cylinder back into the jar, and the jar is then closed. The sample waste is dumped into the outside unit sump at the end of the shift.

6.4 FORMALDEHYDE LOADING

6.4.1 Tank Truck Loading

Tank trucks are loaded by the formaldehyde unit operators during all shifts. Several trucks are loaded each day.

After a truck pulls into the loading rack, the operator opens the top hatch and positions a rigid local exhaust duct approximately six to eight inches above and in the middle of the hatch opening; he then inserts a flexible delivery boom.

Prior to loading, the operator samples the final product storage tank (Figures 3 and 4). This sampling procedure, and analysis of the sample will be described in Section 6.5.

Once the truck sample has been analyzed and meets specifications, the delivery boom and exhaust duct are removed and the hatch is closed. The truck and all contaminated equipment are then hosed off with water to the ground. The operator wears a full-face, acid gas cartridge, approved respirator while withdrawing a storage tank sample and while he is on the loading rack or truck.

6.4.2 Rail Car Loading

Very few rail cars are now loaded at the plant. No rail cars were loaded during the in-depth surveys. As a result, the detailed procedure for rail car loading was not observed. However, verbal description by plant personnel indicates that the rail car loading procedure is almost identical to tank truck loading.

Figure 3. Unit operator sampling tank truck during loading.

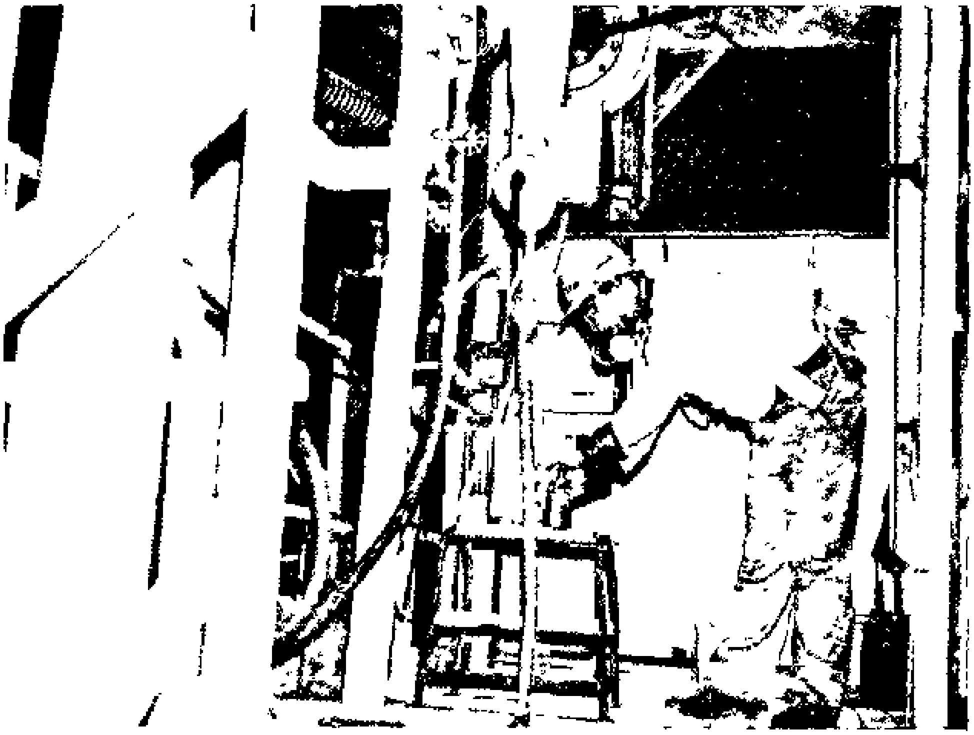

Figure 4. Unit operator with respirator on capping truck sample. Note gloves and sample carrier.

6.5 FORMALDEHYDE SOLUTION SAMPLE WITHDRAWAL AND ANALYSIS

The unit operator samples the absorber twice per shift at the absorber bottoms pump. The sample spigot is a small copper tube, the end of which is approximately two and one-half feet above ground level. Samples are taken in a small narrow-mouth glass bottle (Figure 5).

All purges and waste material are dumped into a covered bucket located approximately 1.5 feet below the sample point (Figure 6). This bucket is dumped into a unit sump, reportedly at the end of each shift.

Each sample is analyzed by the unit operator in the process laboratory building for percent formaldehyde, formic acid, and methanol. For the analysis determining percent formaldehyde, 7 mL of the sample is poured from the 250-mL graduated cylinder into a 10-mL cylinder within a local exhaust ventilated laboratory hood. The 7-mL sample is poured into an open bottle on a scale outside the lab hood. The bottle is weighed; sodium sulfite is added to the bottle to make 150 mL of solution and the solution is automatically titrated outside the hood with hydrochloric acid to determine percent formaldehyde (Figure 7).

Figure 5. Unit operator sampling absorber bottoms. Note gloves and purge bucket.

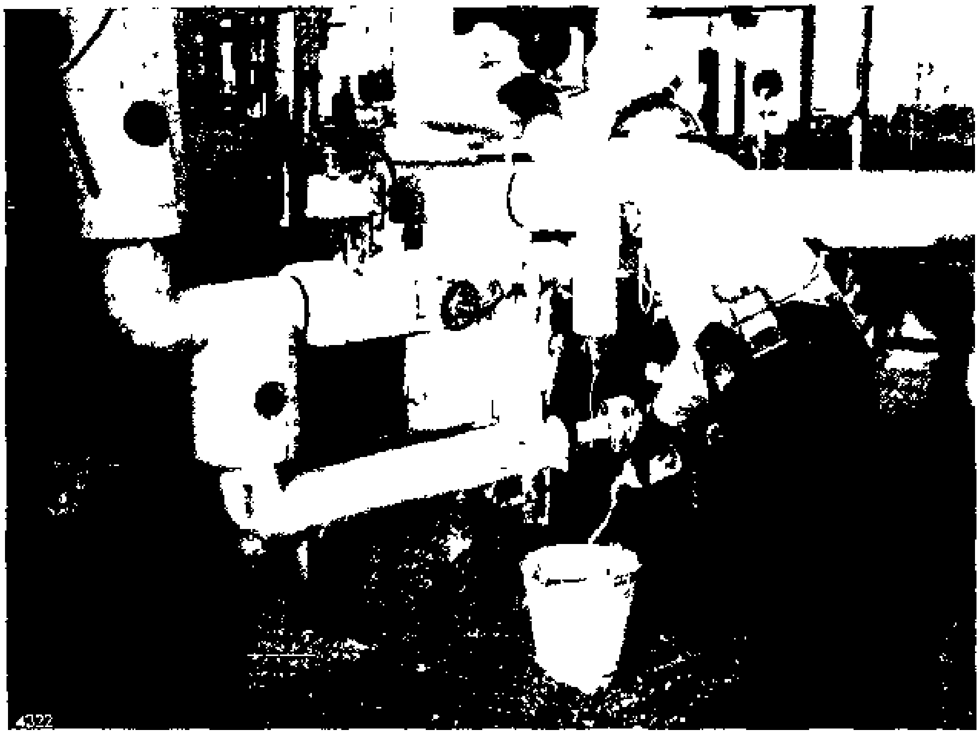

Figure 6. Unit operator pouring bottle purge into bucket.

Next, 10 mL of acetonitrile is added to a 100-mL flask within the lab hood. The process sample is added to the flask in the hood to make 100 mL. Then 5 µL is withdrawn from the flask into a syringe and injected into a gas chromatograph (GC) located outside the hood on the other side of the room.

For the percent formic acid analysis, 40 mL of distilled water is added to a 50-mL graduated cylinder within the hood. Then 10 mL of the process sample is added to the graduated cylinder and the 50 mL solution dumped into a 250-mL beaker within the hood. Indicator is added to the beaker and the solution is manually titrated with sodium hydroxide in the lab hood.

All waste is dumped into an open 500-mL flask in the hood. When the flask is full, the material is dumped in the unit sump outside. The unit operator also collects a sample from the final product storage tank prior to truck loading. The collection point is similar to the absorber process sample point. Purges are poured into a covered bucket below the sample point. When the bucket is filled, the waste is dumped in the unit sump. The sample is taken into the unit control building, and percent formaldehyde and formic acid analyses are performed as described.

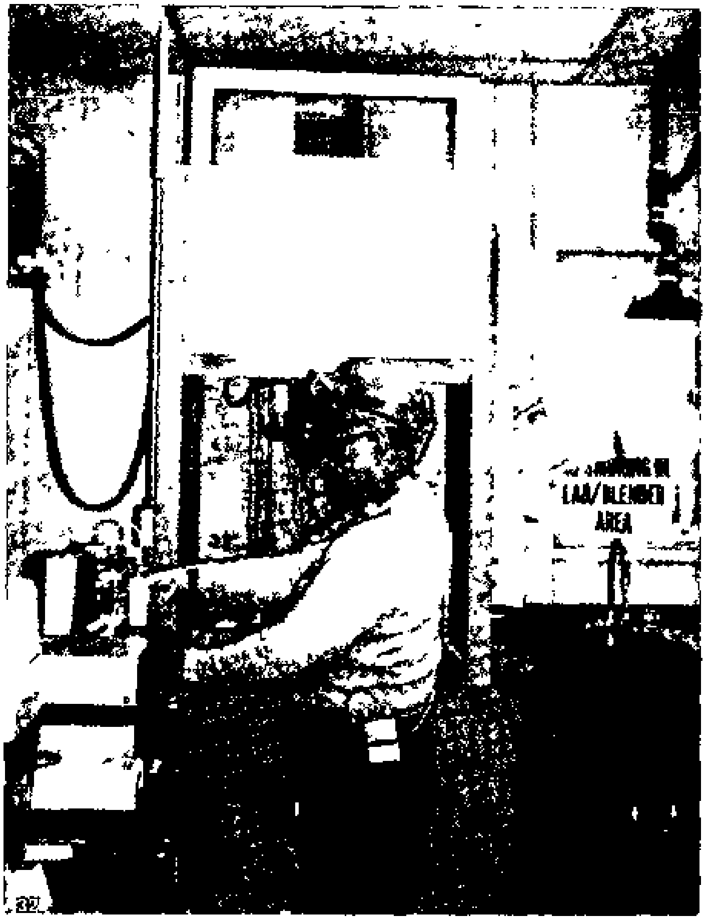

Figure 7. Unit operator setting up percent formaldehyde analysis. Note lab hood and safety shower in background.

A tank truck or rail car sample is obtained after the truck or rail car is approximately half full. A glass jar held at the end of a long rod is inserted through the open hatch or dome, dipped into the solution, and filled. The filled jar is removed and covered with a screw top. The sample is then transported to the unit control building. Percent formaldehyde and formic acid analyses are then performed as described previously. Occasionally a percent methanol analysis may also be run. For some customers half of the truck or rail car samples is taken to the main QC laboratory in another area of the plant for analysis as an audit of the operator results.

7. CONTROL STRATEGY

Several areas of the formaldehyde production operation that present exposure potential are discussed below with respect to the control technology applied. Exposure prevention 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 AREA

Methanol received by the plant is unloaded from a tank truck by the truck driver, who is employed by the methanol distributor, and who is not directly under plant control. The unloading area, as seen in Figure 1, is adjacent to the methanol storage tank, and approximately 150 feet from the production unit and blending/lab area.

The driver chocks the truck wheels, grounds the truck using a small grounding cable, and closes the unloading gate behind the truck (Figure 8). Before unloading, the truck driver opens the tank hatch slightly, leaving a small gap (two to three inches) to allow for air to displace the methanol drained from the tank. This small gap does not present an exposure problem because the suction, created as the tank drains, draws air into the tank and prevents the escape of methanol vapors. The driver then attaches a reinforced, rubber flexible hose with a quick-connect fitting, shown in Figure 9, to the truck discharge port. Figure 10 shows the connected hose. The driver then takes a sample to the operator, who analyzes it. When given approval, the driver returns to start the pump. The methanol is pumped into the adjacent methanol storage tank, shown in Figure 11, using a centrifugal pump with a single mechanical seal with no methanol recycle to the seal. Several trucks were unloaded during the weeks of the surveys. A methanol drip leak occurred during some of the unloading activities and may have affected area sampling and increased the truck driver's exposure.

7.2 METHANOL STORAGE AREA

Methanol is stored in a large storage tank adjacent to the methanol unloading area, as shown in Figure 11. Methanol is delivered to the area by an above-ground pipe and from there to the production unit by an overhead pipe. The storage area is diked and the tank is grounded to reduce accidents. The fluid level of the tank can be

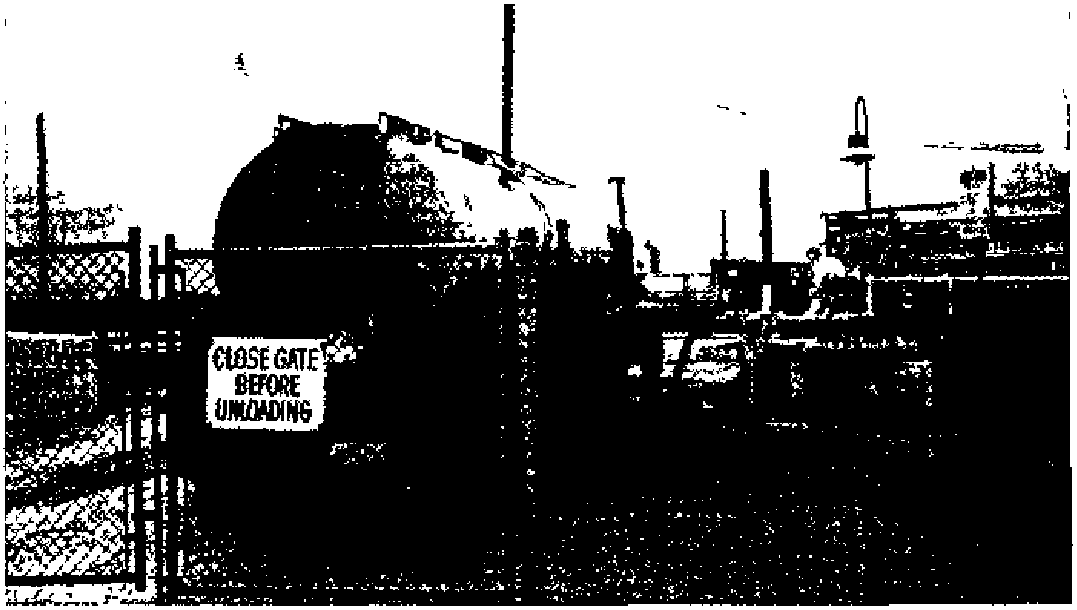

Figure 8. Methanol unloading area. Note gate and warning signs. Truck is in unloading process.

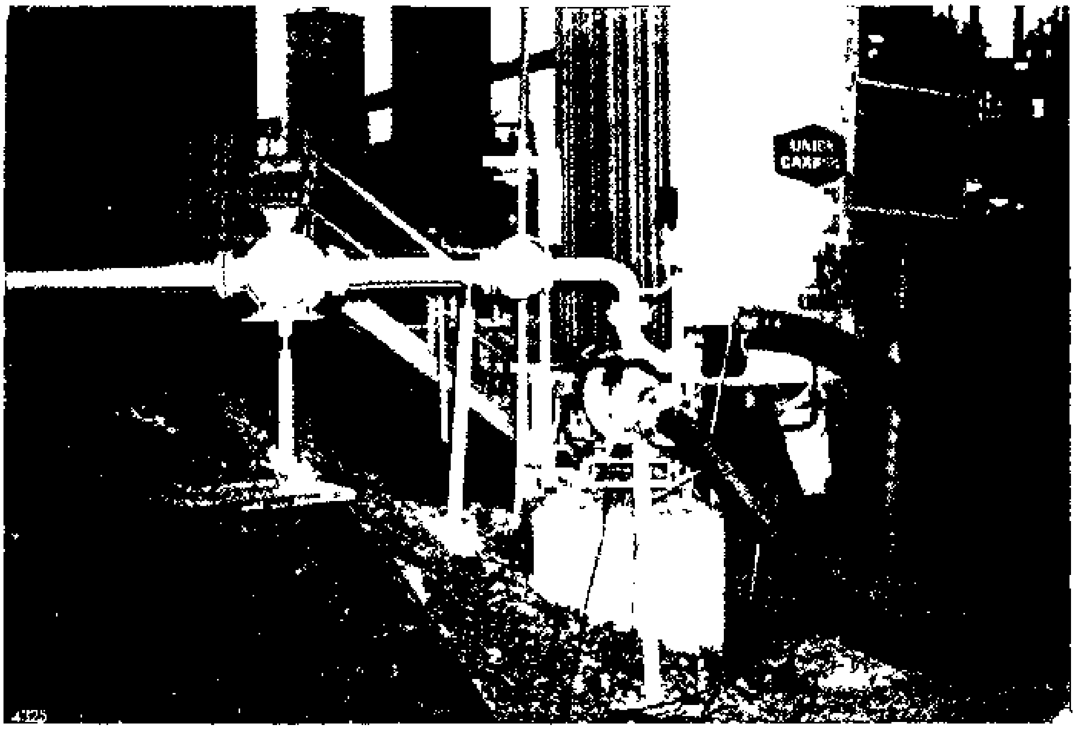

Figure 9. Reinforced rubber flexible hose used for unloading. Note quick-connect and grounding cable.

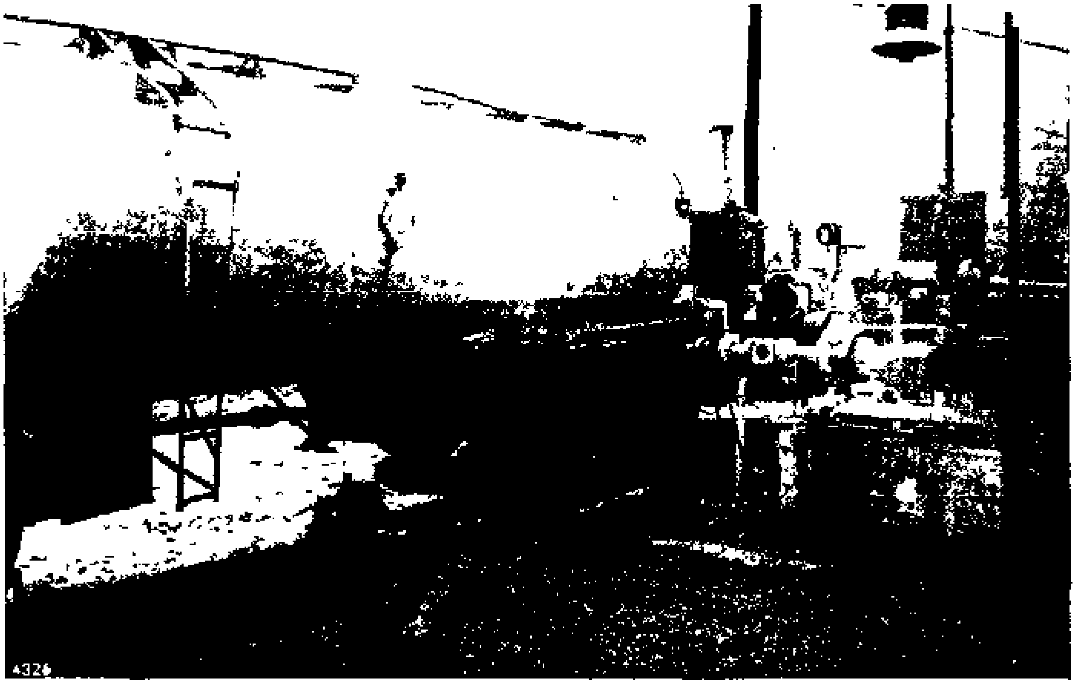

Figure 10. Tank truck connected by unloading hose to unloading pump.

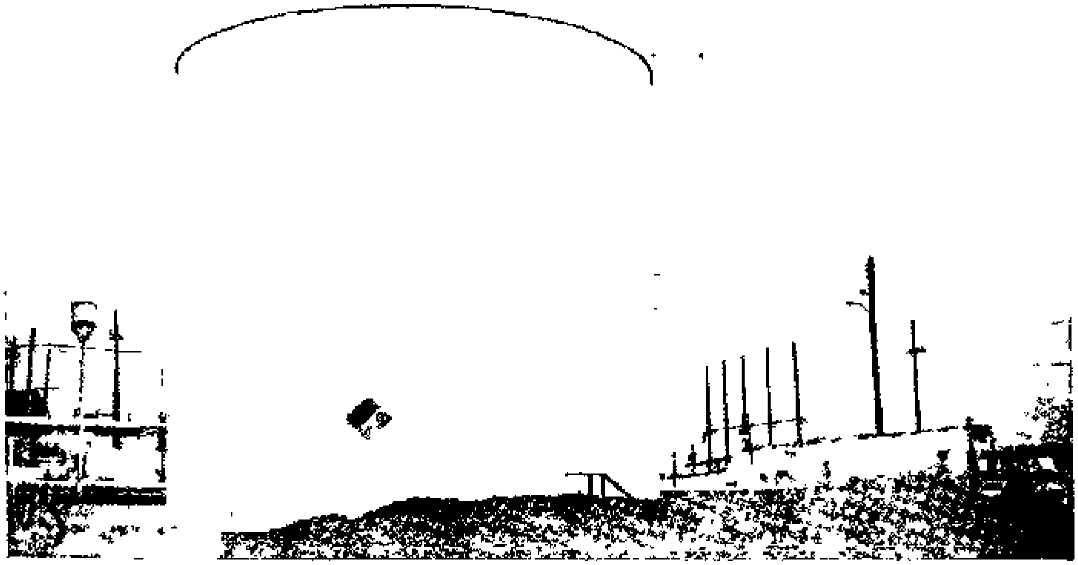

Figure 11. Methanol storage tank. Note dike and delivery truck in unloading area.

checked by an exterior level indicator. The tank has a fixed-roof and is equipped with a flame arrestor. No engineering controls are on the roof to control emissions.

Methanol is pumped from the storage tank to the production unit using one of the three pumps shown in Figure 12. These centrifugal pumps use single mechanical seals with a methanol loop from the pressure side of the pump to help lubricate and flush the seal face.

7.3 CONVERTER AREA

The in-series converters and supporting units are side-by-side in an open air structure as shown in Figure 13. Methanol and air are preheated, mixed, and reacted in a closed system, preventing escape of the reactants. The reactors are equipped with heat exchangers and aftercoolers to recover the waste heat from the reaction, as noted in the process description. Automatic alarms in the control room allow the operators to become aware of system malfunction or situations possibly requiring shutdown. Rupture disks prevent structure damage if a reactor should overpressurize.

Safety showers are located on each floor of the unit. The nature of the enclosed process makes additional engineering controls in this area unnecessary. All valves appear to be well-maintained.

7.4 ABSORBER

Product gas from the converters enters the absorber, where it is quenched with an aqueous formaldehyde solution. The absorber, shown in Figure 14, adjacent to the production unit structure, is a tray column. Gas exiting the top of the absorber contains nitrogen, hydrogen (from the dehydrogenation reaction), and carbon dioxide. It is piped to an afterburner (shown in Figure 15), where a propane-supported flame burns the residual gas to recover its heating value. The remaining nitrogen and carbon dioxide then pass through a waste heat recovery boiler (Figure 16) and are exhausted to the atmosphere through a short stack. Heat recovered as steam is either used within the plant or sold to adjacent plants.

The absorber uses centrifugal pumps with single mechanical seals to circulate the aqueous solution to the trays inside the absorber column. These pumps use the aqueous solution from the pressure side of the pump to lubricate and flush the seal face. Product and bottom recirculation pumps are enclosed in fiber insulation boxes (shown in Figure 17) to prevent freezing and to help maintain the solution temperature, preventing paraformaldehyde formation. A second set of pumps is used to transfer solution to the upper levels of the absorber. No insulation is used on these pumps due to the low concentration of formaldehyde in the solution. Each set of pumps includes a spare pump to allow for continuing operation during pump malfunction.

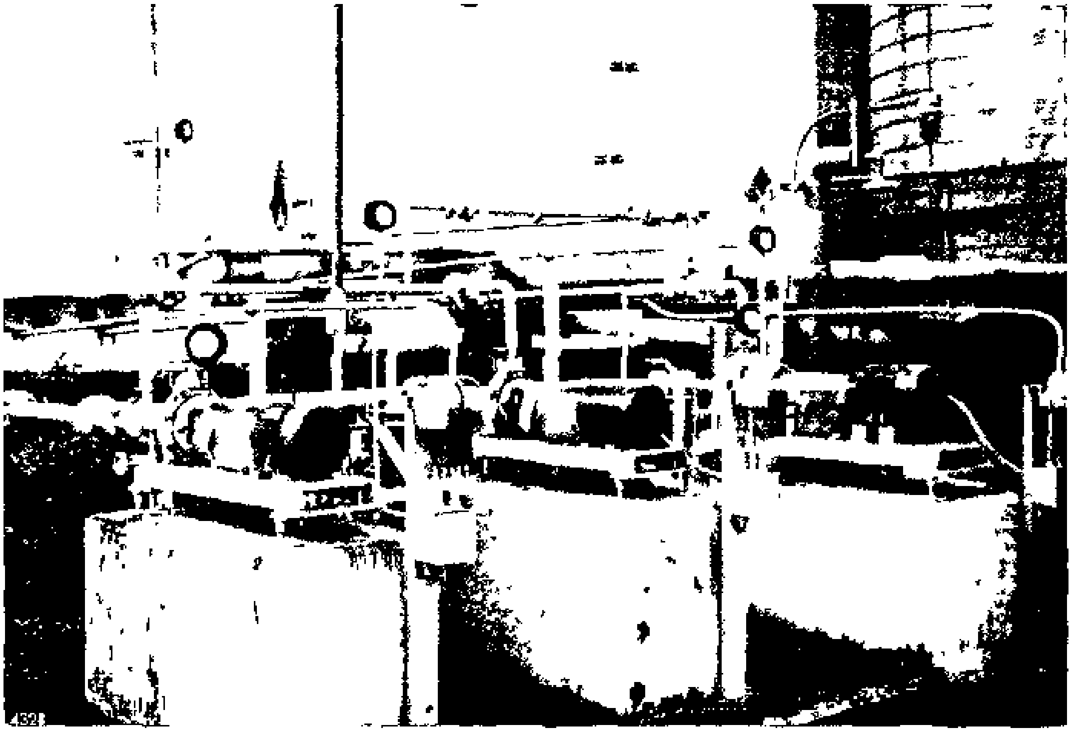

Figure 12. Methanol transfer (supply) pumps. Note safety shower.

Figure 13. Production structure. Both reactors are visible (one left, one right side). Absorber in right background.

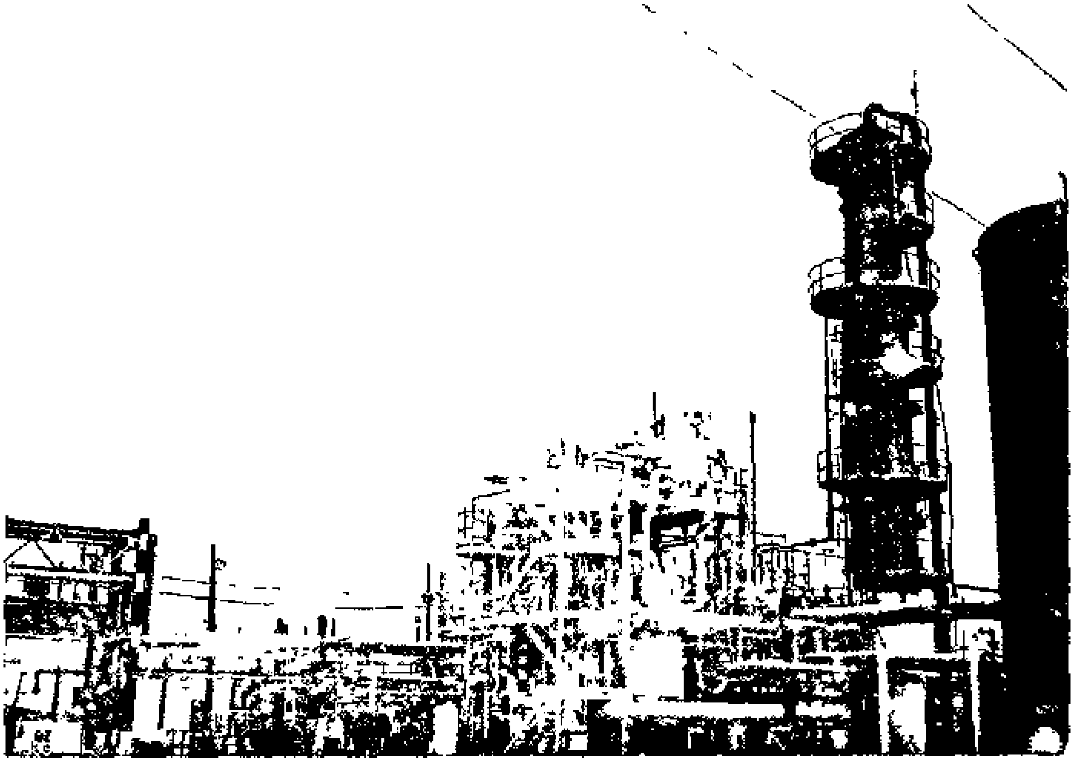

Figure 14. Production structure and absorber; one reactor is visible. Note exhaust gas return line on right side of absorber.

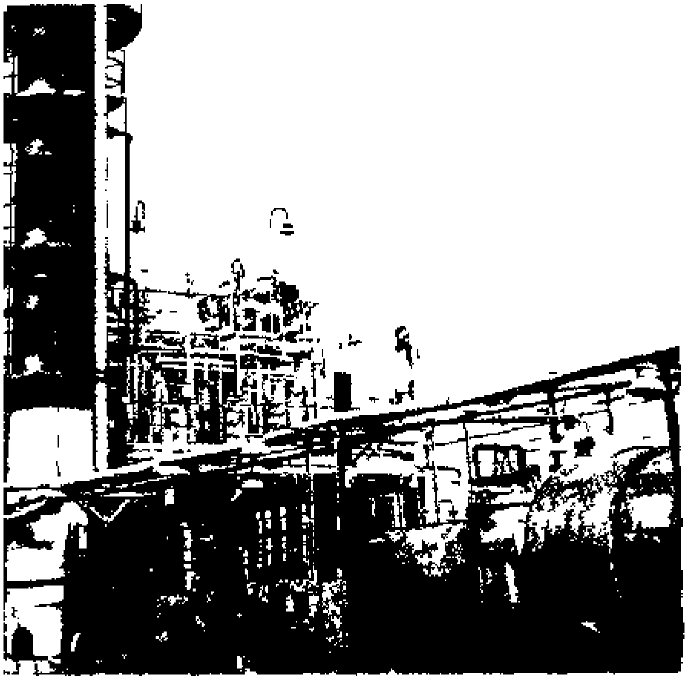

Figure 15. Absorber return line and propane burner used for waste heat recovery.

Figure 16. Waste heat recovery boiler.

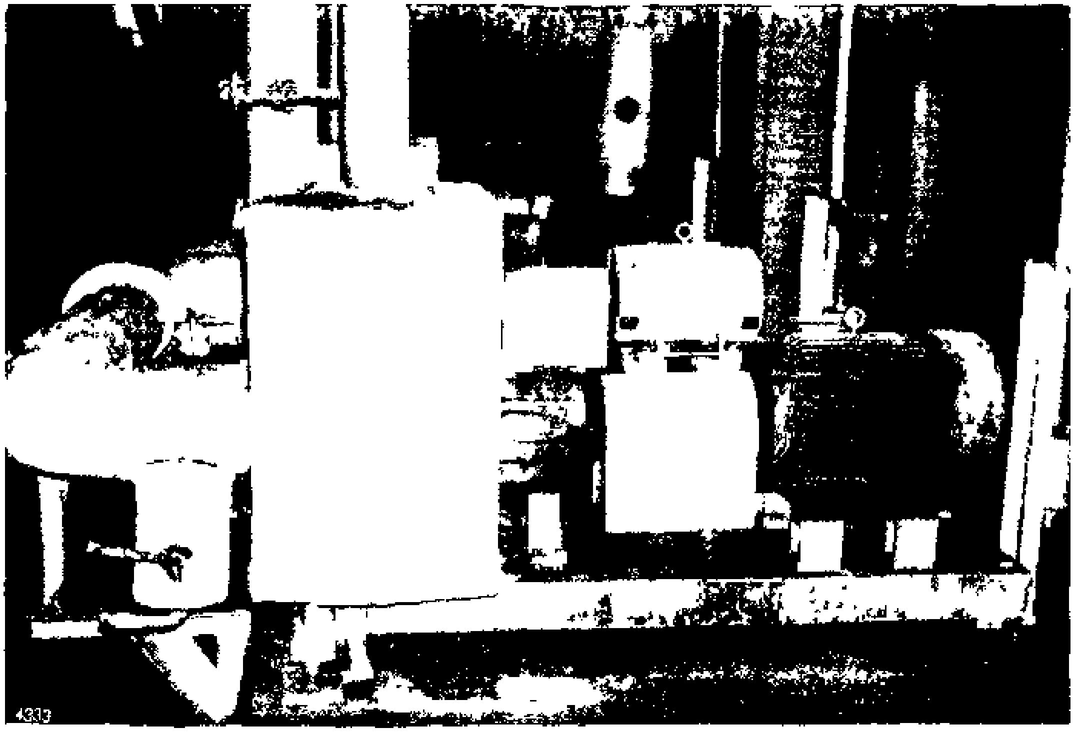

Figure 17. Pump insulation boxes.

Process sampling in this area is conducted every four hours from a point on the product line shown in Figure 18. A small spout on a quick-connect fitting is used. Purge is collected in a covered bucket under the sample point. The sample spout is approximately 1.5 feet from the purge bucket. Splashes in the bucket appear to be common, and splattering can easily occur on windy days, creating a definite potential for contaminating the worker's shoes and clothing. Paraformaldehyde on the cement beside the bucket is evidence of splattering. The covered bucket also creates a direct source of formaldehyde into an area frequented by the operator.

7.5 FORMALDEHYDE STORAGE

Formaldehyde is stored in five grounded tanks inside a diked area, shown in Figure 19. This storage area is adjacent to the blending structure, the truck loading area, and the blending control/laboratory building.

The storage tanks are equipped with steam coils and are insulated to maintain solution temperature and formaldehyde solubility. Centrifugal pumps with single mechanical seals provide agitation to the solution. Formaldehyde solution is used to lubricate and flush the seals on the pumps. External level indicators allow the operator to check solution levels in the tanks with minimal exposure potential. No controls are in place on the vent emissions from the tank. Generally this does not create a significant exposure threat. However, exposure appears to be possible on the third floor of the blending structure, which is on the same level as the tanks. Vents, as shown in Figure 20, are within 20 feet of the structure, and with favorable wind conditions, significant short-term exposure may occur.

7.6 FORMALDEHYDE LOADING

Figure 21 shows the truck loading area for formaldehyde. No rail tank cars are regularly loaded, so this area was not studied. The truck loading area is adjacent to the blending structure and the formaldehyde storage area, and within 100 feet of the blending control/laboratory building. Formaldehyde is loaded into the trucks using the pumps used for agitating the storage tank solution.

Formaldehyde is loaded into tank trucks using a flexible metal hose shown in Figures 22 and 23. In addition, a rigid 6" diameter fiberglass exhaust duct is vertically positioned approximately 6-8 inches above the middle of the open truck hatch. The ventilation system is driven by a blower that was measured in September 1982 by the plant to give 3,500 fpm at the duct opening. Contaminated air is exhausted upwards through a stack at the truck loading rack, which exits approximately 15 feet above the loading rack platform.

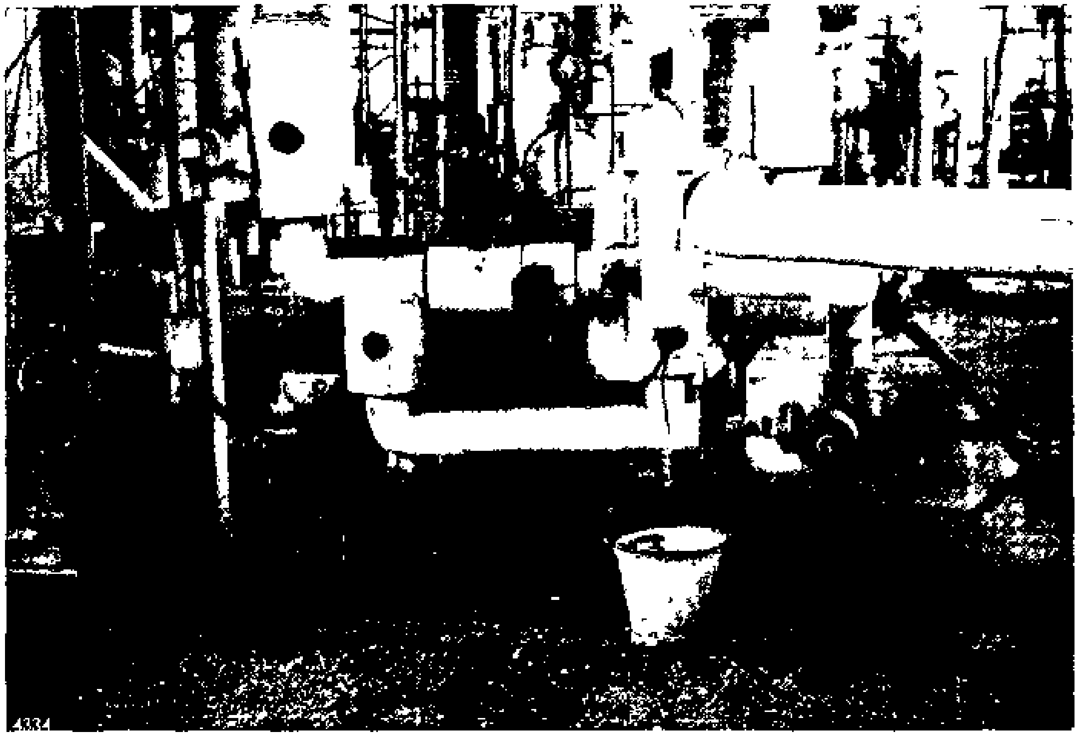

Figure 18. Absorber sample point. Note purge collection bucket and sample spout.

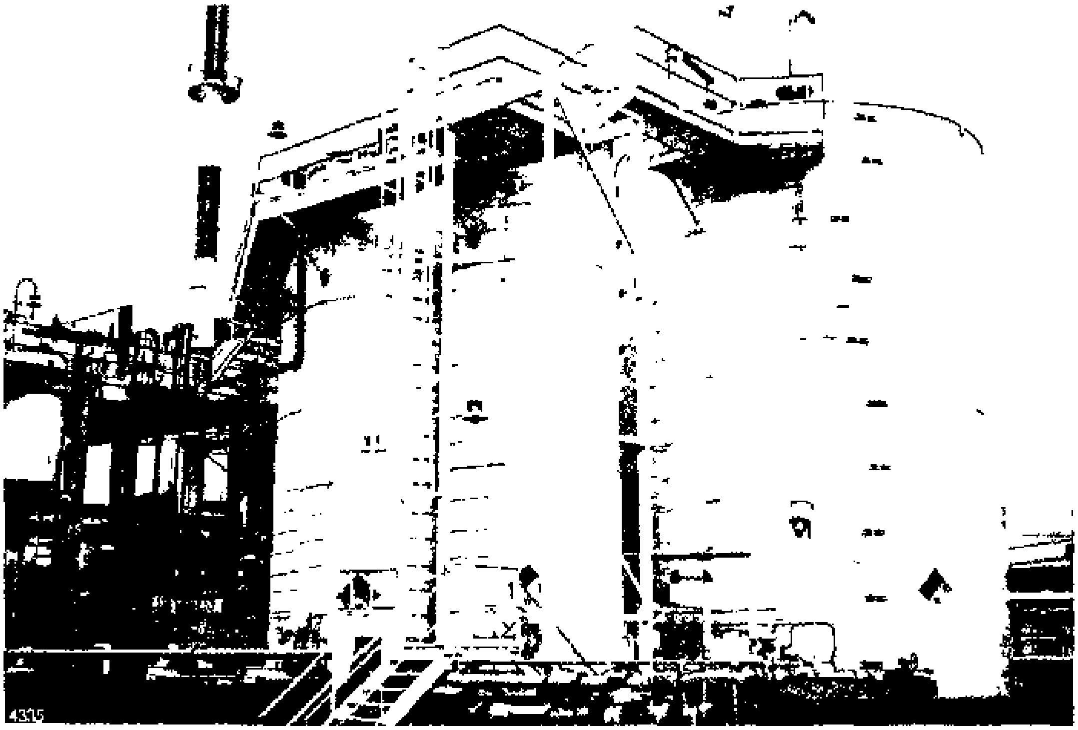

Figure 19. Formaldehyde storage tanks. Note dike and recirculation/loading pumps.

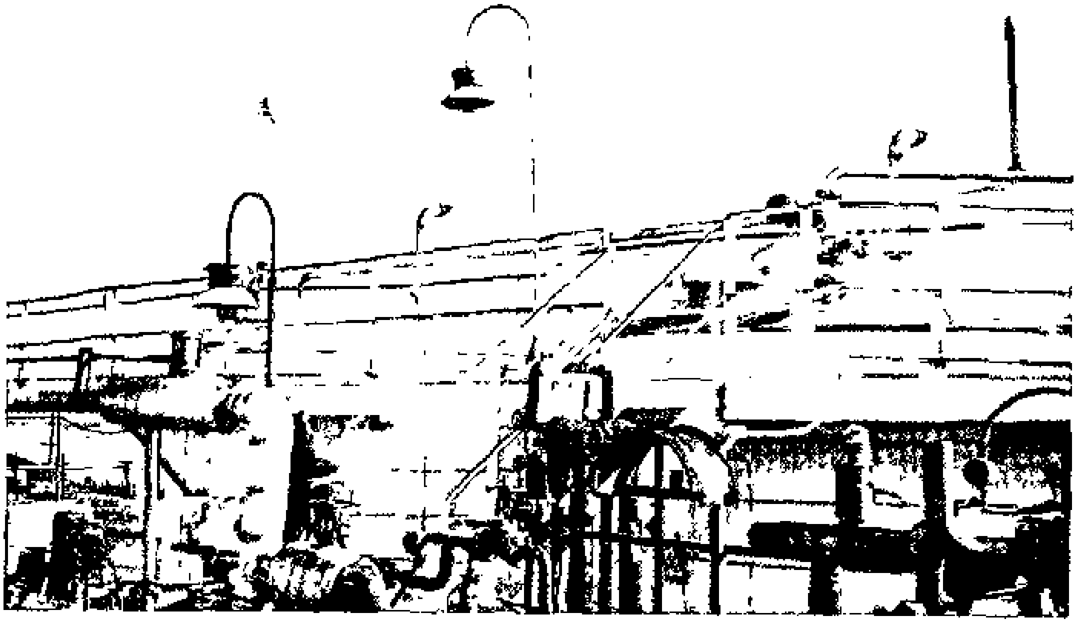

Figure 20. Top of formaldehyde storage tanks. Note proximity of blending structure.

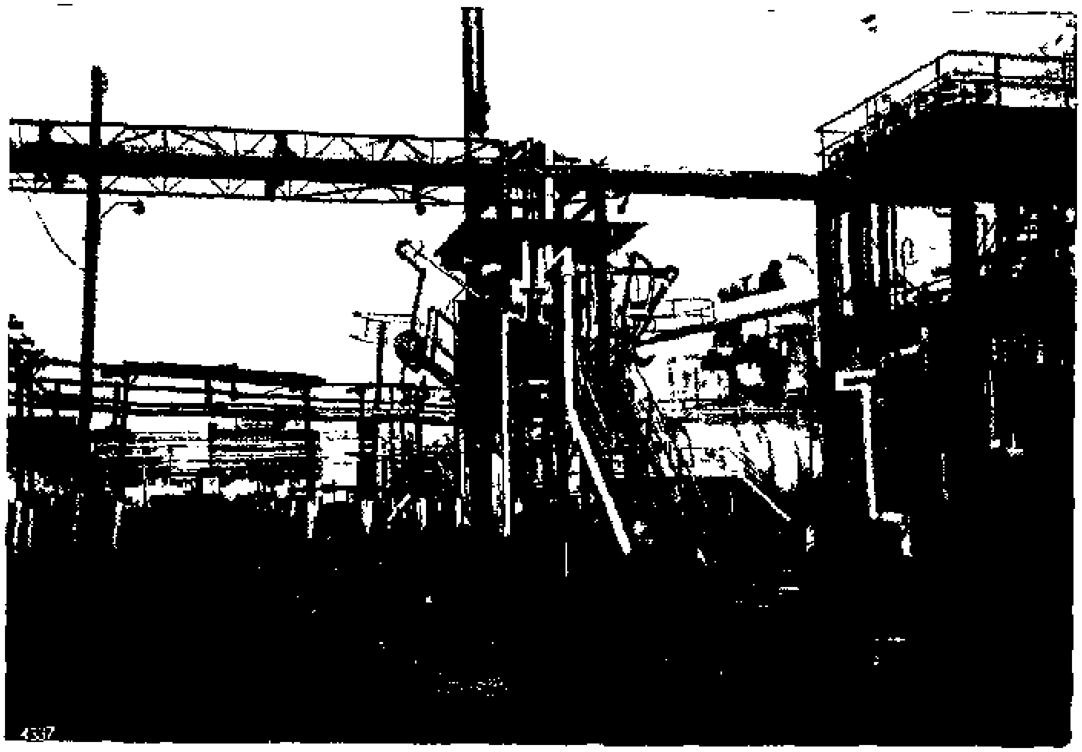

Figure 21. Truck loading area.

Figure 22. Formaldehyde loading. Left, loading spout; right, ventilation duct. Note fiberglass extension.

Figure 23. Formaldehyde loading with ventilation (left) and loading spout (right) in place.

The survey team was unable to obtain velocity measurement either at the duct opening or at the furthest contaminant control point along the edge of the hatch opening; measurements could not be taken since measuring would present an unsafe condition while standing on the edge of the walk to the truck or on the truck.

The industrial hygienist team member did observe local exhaust control capture and concludes that it is adequate. He observed that almost all of the visible condensed water vapor at the hatch opening was captured by the exhaust duct during loading. Visible capture of condensed water vapor from the formaldehyde solution being loaded onto a truck would also indicate capture of nonvisible formaldehyde gas. Personal samples taken on a unit operator during loading and for a full shift indicate a controlled exposure during loading. Better local exhaust ventilation control could be provided by exhausting contaminated air through the exhaust duct which is inserted into the truck tank through a retrofit hatch cover. The cover would have to be vented to prevent a negative pressure within the tank during exhausting.

The blower exhausts the air through a vertical stack, shown in Figure 24. This stack releases the formaldehyde at a sufficient velocity and volume to promote dilution ventilation.

The loading spout, a flexible metal hose, is also placed into the tank. This hose is a forced ventilation duct which draws the vapors from the loading process through a displacement blower and passes it through a packed scrubber shown in Figure 24. This blower appeared to be very effective and no vapors were seen escaping from the open hatch. No cover is used on the hatch.

The loading is controlled by an automatic delivery control device, preventing spills and eliminating manual level checking by the operator. An eyewash and safety shower, shown in Figure 25, were available and clearly marked at the base of the stairs leading to the truck loading platform (approximately 12 feet below the platform).

7.7 CONTROL ROOM

Operators spend most of their time inside the blending control/ laboratory building. Operations are monitored by the chief operator in a second control room across the street from the unit. Communications are generally made by telephone.

Formaldehyde and methanol specific gravity tests are performed within a ventilated laboratory hood (Figure 26) which is vented through the roof. The hood is located in an area easily accessible to the doors and an eyewash/safety shower. A sink is inside the hood to allow wastes from analysis to be safely discarded.

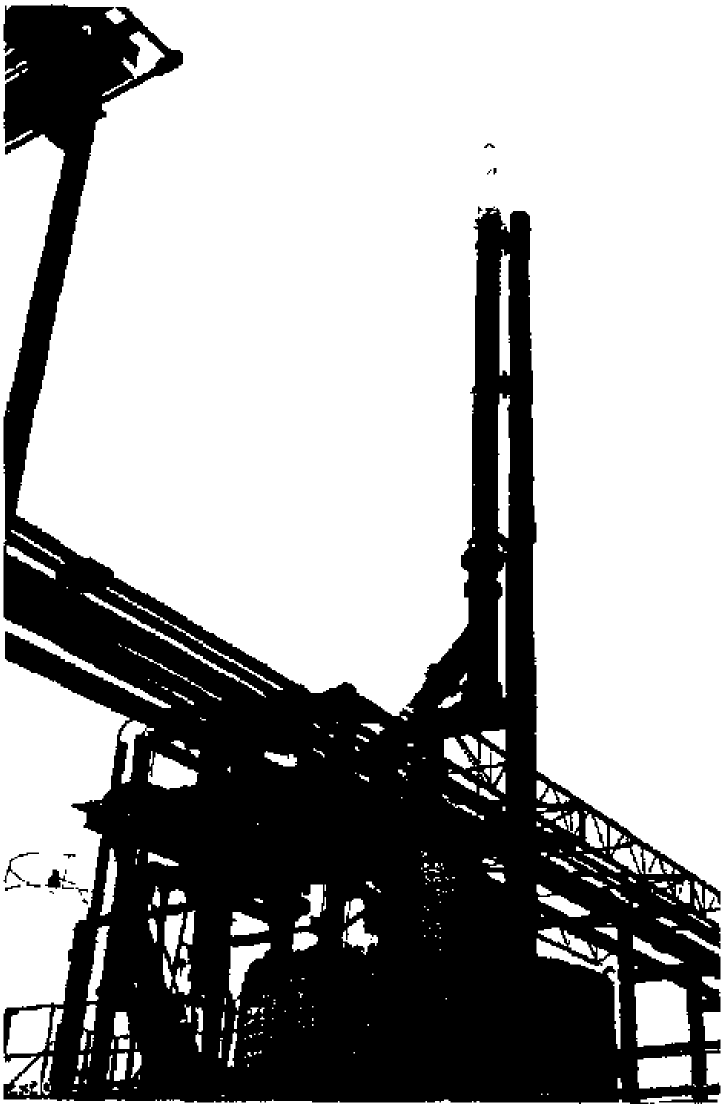

Figure 24. Truck loading ventilation stack.

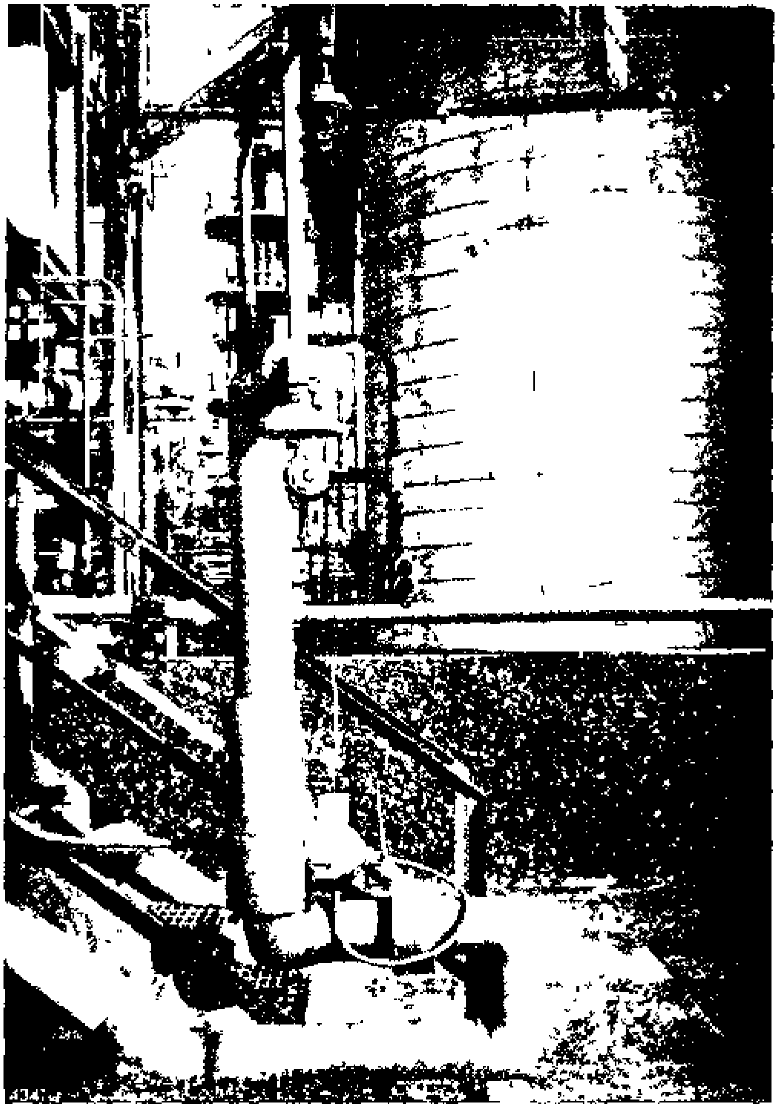

Figure 25. Eyewash and safety shower at truck loading area.

Figure 26. Laboratory hood.

Inward face velocity measurements were made at the open face of the laboratory hood within the unit blending/lab building with an Alnor heated wire anemometer.

The average face velocity was 96 feet per minute (fpm), which should be adequate to control contaminated air resulting from analyses performed in the hood. The American Conference of Governmental Industrial Hygienists recommends a minimum average hood face velocity of 100 fpm to control formaldehyde gas, methanol vapor, and other toxic air contaminants to prevent them from escaping the hood.

Although the blending control/laboratory building is equipped with central air conditioning, this system was not operating properly during most of the survey period. As a result, a pedestal floor fan was being operated within the building. The operation of this fan did cause cross drafts at the lab hood face, temporarily decreasing exhaust control. Proper operation of the existing central air conditioning system would insure better exhaust control at the hood since the system would create less cross drafts.

Although the exhaust is adequate, both the percent formaldehyde titration and sample injection into the GC to determine percent methanol are performed outside the hood. As a result, the hood does not completely control emissions during analysis. See Section 10.1.6 for a description of the exposure due to these analyses being performed outside the lab hood.

8 SAMPLING AND ANALYSIS

Formaldehyde and methanol sampling were conducted during the survey to determine time-weighted average (TWA) long-term and short-term exposure levels (STEL) for personnel and areas associated with formaldehyde production. Two operators were sampled (one for two days, one for three days) for formaldehyde exposure. Four operators were each sampled for one day for methanol. Two chief operators and a production supervisor were also sampled for formaldehyde and three chief operators and a production supervisor were sampled for methanol during eight-hour shifts. These samples were taken to determine the normal 8-hour shift exposure to formaldehyde or methanol. Process operators were also sampled during potentially high exposure activities for short-term exposure levels.

Twelve areas associated with formaldehyde production and frequently attended by the operators, were sampled over an 8-hour shift for formaldehyde and methanol to determine area concentration levels and to possibly pinpoint areas of concern. In addition, three sources of potential emissions (pumps) were sampled to determine their contribution to the area concentration levels. In order to ensure that the 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 sealed with tape. The concentration levels in the source samples were assumed to correspond to the amount of agent released by the sources over the sampling period and were then translated into the amounts of pollutant released per day.

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 the time-weighted average exposures Short-term samples, collected over periods of between 15 and 120 minutes, were used to determine the exposures from certain but typically short events occurring during normal regular shift hours. Personal long-term samples generally were comprised of two, approximately 240 minutes long, consecutive sampling periods and were used to determine an eight-hour, time-weighted average according to the following formula:

$$TWA = \frac{T_1X_1 + T_2X_2}{T_t} \qquad \text{Ref. [2]}$$

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 as well as area samples. Long-term samples were repeated on a second day to enhance the survey results and to evaluate day-to-day variations in reproducibility.

Short-term samples were taken during operator activities where peak exposures might be expected, but possibly not be shown in the long-term samples. The short-term samples were also to indicate where controls may be more cost-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 pollutant volume sufficient for reliable analysis.

8 2 SAMPLING METHODS

Sampling for formaldehyde was conducted using an active dosimeter method developed by the research department of Monsanto Agricultural Products Company [3] and approved by the NIOSH project officer, Mr. W. N. McKinnery, Jr. The method uses sampling tubes packed with 2,4-Dinitrophenylhydrazine (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 set and calibrated to deliver a constant flow rate (±5%) of approximately 100 cm^3/min (actual pumps ranged from 92.0 to 115.5 cm^3/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 cm^3/min (actual pumps ranged from 180.7 to 203.4 cm^3/min). Pumps were generally checked for significant (greater than ±5%) deviation after use, and the samples were discarded where a significant deviation was observed.

To assure quality of results, formaldehydehyde 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 A.

Sampling for methanol was conducted using a NIOSH-approved active dosimeter method, NIOSH S59. 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 cm^3/min (actual flows varied between 47.5 and 56.8 cm^3/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 and the results reported according to MRC Quality Assurance/Quality Control Procedures. Additional details on the methanol sampling and analysis procedures used in these surveys are included in Appendix A

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 flow, sampling time, and comments.

8.3 NUMBER OF SAMPLES

Excluding blanks and spikes, 60 formaldehyde and 38 methanol samples were collected during the survey as shown in Table 1, Section 1 2.

8.4 LOCATIONS SAMPLED

Figure 27 shows the location in the plant where sampling was conducted Table 2 lists the locations sampled and the number of samples of each type taken at each location.

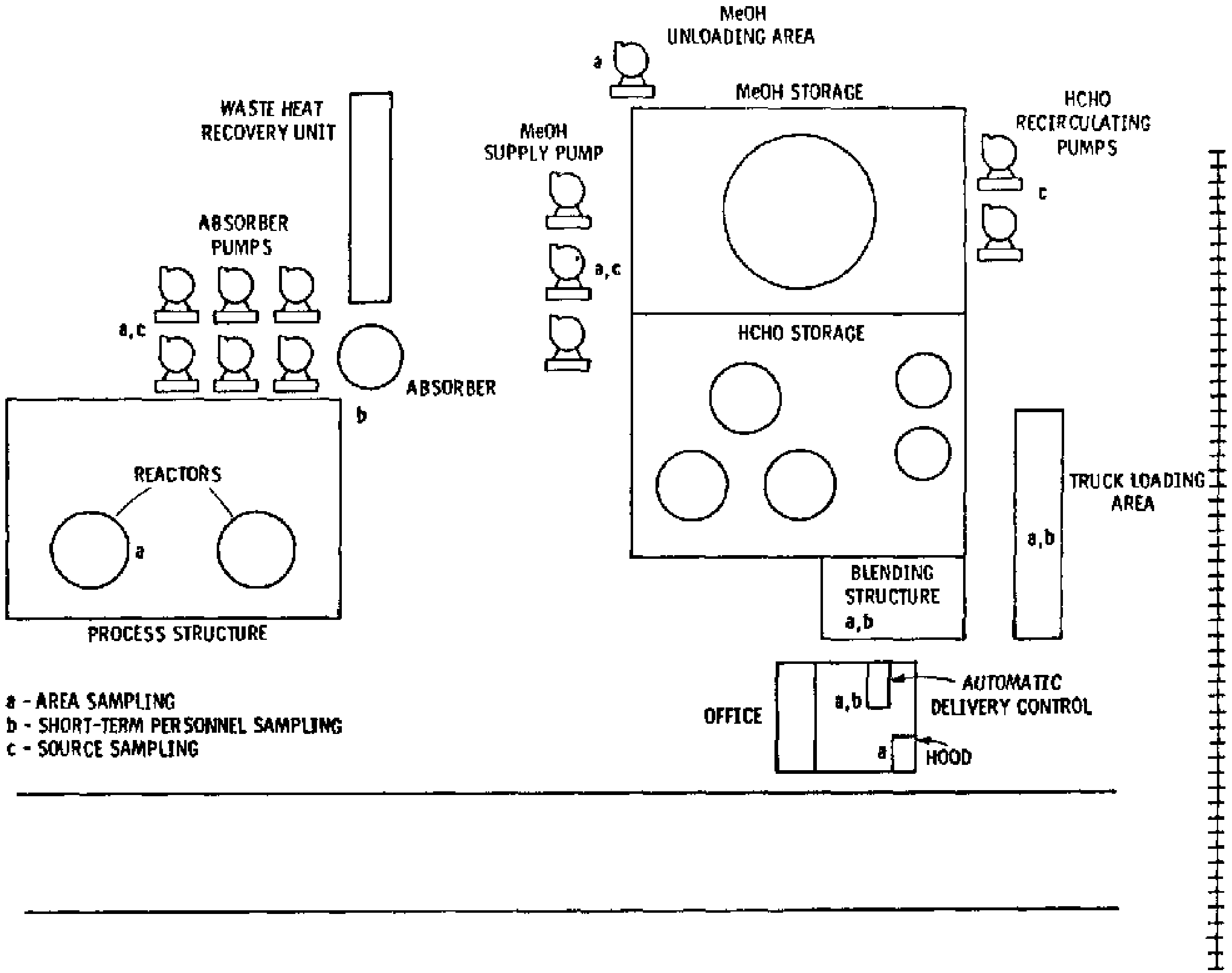

Figure 27. Locations of area, short-term personal, and source sampling conducted during the survey.

TABLE 2 AREA AND SOURCE SAMPLE NUMBER AND LOCATION SUMMARY

Location	Number of samples	
	Formaldehyde	Methanol
Area		
Primary reactor - ground floor	7	2
Primary reactor - 2nd floor	2	2
Absorber	2	2
Blending area - ground floor	-	3
Formaldehyde storage - west of tanks	2	1
Formaldehyde storage - between tanks	2	1
Methanol supply pump	-	3
Blending area - 3rd floor	2	
Truck loading	3	
Blending control/lab building	6	4
Blending control/lab hood	4	
Methanol unloading		3
Source		
Absorber bottom pump	2	
Agitation/loading pump	2	
Methanol supply pump		2

9 RESULTS

The following tables present the analytical results for samples taken by the MRC survey team at the DuPont Grasselli-Linden, New Jersey plant during October 25-29, 1982 and June 14-16, 1983. All volumes and concentrations have been corrected to standard temperature and pressure (20°C and 760 torr or 68°F and 29.92 in. 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 personal methanol samples were taken Area sample results are presented in Tables 6 and 7. Source sample results can be found in Table 8.

TABLE 3 LONG-TERM FORMALDEHYDE PERSONAL SAMPLE ANALYTICAL RESULTS

Description	Day	Shift	Tube number	Flow rate[a] cc/min	Sample time, min	Adjusted volume[b] (V) L	Concentration, (C) ppm	Consecutive sampling period, min	8-hr TWA, ppm	Personal average[c] ppm
Operator 1	6/14	1	1812	92.1	120	10.7	0.56	120	0.56	
	6/15	1	1278	101.4	199	19.4	0.40			
	6/15	1	1786	100.3	185	17.9	0.42	384	0.41	
	6/16	1	1914	113.5	178	19.5	0.09			
	6/16	1	148	106.1	139	14.1	0.13	317	0.11	0.31
Operator 2	6/14	2	1083	104.8	198	20.5	0.46			
	6/14	2	1963	94.4	141	13.1	0.27	339	0.39	
	6/15	2	1718	99.0	187	18.1	0.11			
	6/15	2	1261	102.2	173	17.3	0.36	360	0.23	0.31
Chief operator 1	6/16	1	1796	102.4	176	17.3	0.23			
	6/16	1	1797	112.7	165	17.9	0.25	341	0.24	0.24
Chief operator 2	6/14	2	420	101.0	196	19.5	0.18			
	6/14	2	1161	103.2	136	13.8	0.27	332	0.22	
	6/15	2	1919	108.0	209	22.1	0.20			
	6/15	2	1984	100.5	170	16.7	BDL	379	<0.13	<0.17
Production supervisor	6/14	1	1141	126.2	201	24.6	0.21			
	6/14	1	1720	105.0	155	15.8	0.46	356	0.30	
	6/16	1	1850	95.7	151	13.8	0.32	151	0.32	0.31

[a] Flow rate determined as follows ±5% deviation from original flow rate assume initial flow rate, >5% deviation, average initial and final flow rates

[b] Volume adjusted to standard conditions (68°F, 29.92 in Hg, 20°C, 760 torr)

[c] Average concentration = $(V_1 C_1 + V_2 C_2 + \quad)/(V_1 + V_2 + V_3 \quad)$ - overall values for that worker

TABLE 4. METHANOL PERSONAL SAMPLE ANALYTICAL RESULTS

Description	Day	Shift	Tube number	Flow rate,[a] cc/min	Sample time, min	Adjusted[b] volume, (V) L	Concentration, (C) ppm	Consecutive sampling period, min	8-hr TWA ppm	Personal average,[c] ppm
Operator 1	10/26	1	14	50 8	191	10 28	BDL[d]			
	10/26	1	20	50 8	182	9 80	BDL	373	BDL	BDL
Operator 2	10/25	2	05	48 8	166	8 74	BDL			
	10/25	2	08	48 8	111	5 85	BDL	277	BDL	BDL
	10/25	2	07	48 8	Void	TUBE BECAME DISCONNECTED - 08 REPLACES IT				
Operator 4	10/27	2	35	50 7	227	12 21	0 84			
	10/27	2	39	50 7	191	9 72	1 73	418	1 25	1 25
Operator 5	10/28	1	40	54 7	192	10 75	>2 02[e]			
	10/28	1	45	54 7	214	11 99	0 61	406	>1 28	>1 28
Production supervisor	10/26	1	10	48 0	204	10 37	BDL			
	10/26	1	22	48 0	203	10 32	BDL	407	BDL	
	10/28	1	41	51 2	221	11 59	>10 57[e]			
	10/28	1	51	51 2	204	10 69	BDL	425	>0 44	>0 37
Chief operator 1	10/26	1	13	50 0	196	10 38	BDL			
	10/26	1	23	50 0	180	9 54	0 35	376	0 32	0 32

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[a] Flow rate determined as follows ±5% of initial flow rate, assume initial flow rate, >±5% deviation, average the two flow rates

[b] Volume adjusted to standard conditions (68°F, 29 92 in Hg)

[c] Personal average - overall values for that worker = $(V_1 C_1 + V_2 C_2 + \quad)/(V_1 + V_2 + \quad)$

[d] BDL >0 3 ppm

[e] Breakthrough occurred - minimum concentration

TABLE 5. SHORT-TERM FORMALDEHYDE PERSONAL SAMPLE ANALYTICAL RESULTS

Description	Day	Shift	Tube number	Flow rate,[a] cc/min	Sample time, min	Adjusted volume,[b] (V) L	Concentration, (C) ppm	Personal average, ppm	Activity average, ppm
Process sampling and analysis									
Operator 1	6/15	1	1987	189 2	16	2 9	0 79		
	6/16	1	1967	206 6	13	2 6	BDL	<0 51	
Operator 2	6/14	2	1764	208 1	16	3 3	1 56		
	6/14	2	86	208 1	16	3 3	0 54		
	6/15	2	414	187 8	15	2 7	1 42		
	6/15	2	1209	187 8	14	2 5	1 76	1 28	<1 04
Truckloading									
Operator 1	6/15	1	1274	111 0	62	6 6	0 96		
	6/16	1	1834	99 7	31	3 0	1 79	1 22	1 22

[a] Flow rate determined as follows ±5% deviation from original flow rate, assume initial flow rate, >±5% deviation, average the flow rates

[b] Volume adjusted as standard conditions (68°F, 29 92 in Hg, 20°C, 760 torr)

[c] Average of all individual workers exposure

TABLE 6. FORMALDEHYDE AREA SAMPLE ANALYTICAL RESULTS

Description	Tube number	Flow rate,[a] cc/min	Sample time, min	Adjusted volume,[b] L	Concentration, ppm	Area TWA,[c] ppm
Primary reactor - 1st floor	1217	97.2	273	25.6	0.04	
	80	101.0	224	21.9	0.16	
	1215	109.2	234	24.7	3.63	
	1924	113.9	173	18.9	0.95	
	1936	101.3	170	16.5	BDL[d]	
	20	99.2	150	14.3	0.16	
	1294	98.7	183	17.4	0.65	<0.92
Primary reactor - 2nd floor	1088	104.4	277	27.9	0.06	
	70	103.8	235	23.6	0.09	0.07
Absorber	1859	99.5	273	26.3	0.09	
	1993	100.3	227	22.0	0.58	0.31
Blending structure - 3rd floor	428	102.0	241	23.6	0.16	
	129	99.8	254	24.3	0.11	0.13
HCHO storage - west of tanks	381	104.4	240	24.0	0.35	
	35	99.5	253	24.2	0.22	0.28
HCHO storage - between tanks (central)	1159	116.8	241	27.1	0.17	
	1708	94.4	262	23.7	0.22	0.19
Truck loading	272	101.1	67	6.6	BDL	
	1145	110.5	42	4.4	BDL	
	297	115.2	28	3.0	1.55	<0.40
Blending control/lab building	1025	112.9	188	20.5	0.52	
	1866	99.9	187	18.1	0.69	0.60
	418	101.4	159	15.5	0.13	
	34	115.2	183	20.3	0.22	0.18
	1758	96.3	241	22.9	0.48	
	32	103.0	131	13.3	0.23	0.39
Blending control/lab hood	1809	182.4	9	1.6	2.60	
	1744	211.2	11	2.2	1.90	2.19
	1186	209.7	15	3.1	0.53	
	1923	209.5	14	2.8	1.51	1.00

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[a] Flow rate determined as follows ±5% deviation of original flow rate, assume initial flow rate, >±5% deviation, average the flow rates.

[b] Volume adjusted to standard conditions (68°F, 29.92 in Hg, 20°C, 760 torr)

[c] Area TWA = $(V_1 C_1 + V_2 C_2 + \ldots)/(V_1 + V_2 + \ldots)$.

[d] BDL <0.05 ppm.

TABLE 7. METHANOL AREA SAMPLE ANALYTICAL RESULTS

Description	Tube number	Flow rate,[a] cc/min	Sample time, min	Adjusted volume,[b] L	Concentration, ppm	Area TWA,[c] ppm
Primary reactor - 1st floor 2 ft above ground	48/48A[d]	47.5	266	12.94	0.90	
	55	47.5	248	12.35	BDL[e]	0.61
Primary reactor - 2nd floor BZH	49/49A[d]	51.4	275	14.48	>13.70[f]	
	52	51.4	232	12.50	0.47	>7.65
Absorber - 5 ft from absorber, 3 ft from circulation pump	47/47A[d]	49.3	251	12.66	0.89	
	53	49.3	243	12.56	BDL	0.55
Blending area	16	50.0	242	12.82	BDL	
	15	50.0	231	11.96	BDL	
	31	53.2	230	12.98	0.53	0.37
HCHO storage area - west of tanks	36	54.5	228	13.78	1.37	1.37
HCHO storage area - central	33	51.2	232	12.60	0.85	0.85
MeOH unloading area	29	55.5	54	3.15	BDL	
	34	53.2	48	2.70	5.7[f]	
	44	56.8	65	3.78	>3.6[f]	3.11
Central room - BZH	12	51.2	191	10.36	BDL	
	21	51.2	214	11.61	BDL	
	43	49.5	191	9.67	>0.86[f]	
	50	49.5	214	10.84	0.28	>0.42
MeOH supply pump area	17	54.9	232	13.50	BDL	
	26	54.9	221	12.56	BDL	
	38	52.5	236	13.14	>5.0[f]	>1.88

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[a] Flow rate determined as follows ±5% deviation of original flow rate, assume initial, >±5% deviation average the two flow rates

[b] Adjusted as standard conditions (68°F, 29.92 in Hg, 20°C, 760 torr)

[c] Average = $(V_1 C_1 + V_2 C_2 + \quad)/(V_1 + V_2 + \quad)$

[d] Two tubes in series used concentration added

[e] BDL >0.3 ppm

[f] Breakthrough occurred - minimum concentration

TABLE 8. SOURCE SAMPLE ANALYTICAL RESULTS

Description	Tube number	Flow rate,[a] cc/min	Sample time, min	Adjusted volume,[b] L	Concentration, ppm	Average concentration,[c] ppm
Formaldehyde						
Absorber bottom pump	1929	105 6	51	5 4	115	
	127	105 6	31	3 3	142	125
HCHO agitation/loading pump	1862	94 4	51	4 8	18 7	
	85	94 4	28	2 6	20 2	19 2
Methanol						
MeOH supply pump	32	50 7	111	6 01	21 4	
	42	50 7	118	6 34	13 95	17.58

[a] Flow rate determined as follows ±5% deviation of original flow rate, assume initial, >±5% deviation - average the two flow rates

[b] Adjusted as standard conditions (68°F, 29.92 in Hg, 20°C, 760 torr).

[c] Average = $(V_1 C_1 + V_2C_2 + \quad)/(V_1 + V_2 + \quad)$.

10. CONCLUSIONS

10 1 FORMALDEHYDE EXPOSURE

10 1 1 Supervisor Long-Term Exposure

Two sets of long-term consecutive personal samples were taken on the production supervisor during two day shifts. One sample of the set taken on 6/15 had to be voided. Results are presented in Table 3, Section 9. The time-weighted average (TWA) concentration for the set of samples taken on 6/14 gives a good estimate of this worker's TWA exposure over the entire shift. The TWA of 0.32 ppm for this set of samples was less than 11% of the OSHA TWA permissible exposure limit (PEL) of 3 ppm, indicating a nonexcessive exposure for that sampling day Thus, although the production supervisor occasionally inspects formaldehyde unit operations, his exposure is probably not great enough to cause an excessive long-term exposure

The overall supervisor for the formaldehyde and sulfuric acid units should also have a nonexcessive exposure, based on a comparison of his activities compared to those of the production supervisor. No personal samples were taken from this overall supervisor. However, since the overall supervisor spends a majority of his time in his separate office or in other areas away from the units, and not in the process unit area, his exposure is likely to be less than that of the production supervisors.

10 1 2 Chief Operator Long-Term Exposure

Three sets of consecutive long-term personal samples were worn by three chief operators during a workshift. Results can be found in Table 3, Section 9. The TWA concentrations for each set of samples, which ranged from 0.12 to 0.24 ppm, should give a good estimate of a chief operator's 8-hour shift exposure. These results are equal to or less than 8% of the OSHA TWA PEL of 3 ppm. Thus, the chief operator exposure can be considered nonexcessive for those days sampled.

10.1.3 Formaldehyde Unit Operator Long-Term Exposure

Two consecutive long-term personal samples were obtained for unit operators on five different shifts. One of the long-term samples worn on 6/14 had to be voided due to pump failure. Analytical data are presented in Table 3, Section 9. TWA concentrations for the four sets of samples should give a good indication of the unit operator TWA exposure for the entire 8-hour shift. The TWA concentrations for the four sets of samples ranged from 0.11 to 0.41 ppm.

The sample results are equal to or less than 14% of the OSHA TWA PEL These results indicate that the unit operator was not exposed to an excessive formaldehyde gas exposure, using the OSHA TWA PEL as the reference standard.

In addition to the personal samples taken during the survey, three sets of area samples were taken in the lab area of the blending control/lab building. Analytical results are presented in Table 6, Section 9. These sets of samples indicate a TWA concentration for an area in which the unit operator spends a considerable portion (approximately 50%) of his time. TWA concentrations ranged from 0 18 to 0 61 ppm. This indicates a relatively low exposure within the blending control/lab building, which is due to sample analyses and the unit exposure outside the building.

10 1.4 Maintenance Personnel Long-Term Exposure

It was not possible to take long-term personal samples on process mechanics or service operators while repairing equipment at the formaldehyde unit. None of these workers were repairing equipment at the formaldehyde unit during the survey.

It is expected that repairs of major liquid or gaseous leaks could cause both short-term or long-term excessive exposures for maintenance workers. Temporary controls are then provided through the required wearing of a self-contained breathing apparatus and gloves for major leaks.

10 1.5 Formaldehyde Loading

Three short-term personal samples were taken on a unit operator while performing duties required to load a tank truck. One sample had to be voided In addition, three area samples were taken on the truck loading rack during loading. Since no rail car loading was being performed during the survey week, sampling could not be conducted to assess the exposure in this operation. Sample data for the personal samples are shown in Table 5, Section 9; data for the area samples are given in Table 6, Section 9.

The personal sample results were 0.96 and 1.79 ppm. Both personal sample concentrations are less than the OSHA ceiling limit of 5 ppm and indicate a non-excessive short-term exposure during truck loading using the OSHA ceiling limit as a reference. Also, the unit operator is provided protection while on the loading rack and truck, and sampling by the wearing of a respirator. According to the supplier (MSA), the acid gas cartridge being used at this plant has been approved by NIOSH for formaldehyde service

The area samples taken on the truck loading rack ranged from two concentrations which were below the analytical detection limit up to 0.76 ppm. These concentrations plus the personal sample concentrations indicate adequate local exhaust ventilation at the hatch during loading.

10.1.6 Formaldehyde Solution Sample Withdrawl and Analysis

Six personal samples were taken for unit operators during six separate absorber sample collections and analyses. The sample concentrations ranged from a BDL concentration to 1.76 ppm. Sample data are shown in Table 5, Section 5.

All of these concentrations are below the OSHA ceiling limit of 5 ppm, indicating a non-excessive short-term exposure during absorber sample collection and analyses. These results indicate that the formaldehyde gas exposure resulting from the percent formaldehyde titration and percent methanol determination using the GC outside the lab hood do not present significant enough uncontrolled exposures to cause an overexposure for the operator for the entire withdrawl and analysis process. Also, it appears that withdrawing of a sample without the use of engineering exposure controls does not present an excessive exposure. The operator is offered control through the wearing of a respirator during sample withdrawal.

Four area samples were taken at the lab hood during sample analyses to determine the extent of exposure during the percent formaldehyde titration performed outside the hood. It was speculated that formaldehyde gas would pass from the formaldehyde titration setup past the samples to the lab hood. If the short-term personal samples were high and the results were high for the hood area samples, one could conjecture that a major source was due to the uncontrolled formaldehyde titration. Since the personal samples are considered non-excessive, conclusions regarding the area results are not needed.

10.1 7 Formaldehyde Area Sampling

Consecutive 4-hour area samples were collected in six locations in the formaldehyde process unit and storage area in addition to the areas discussed earlier. Sample times ranged from 150 to 273 minutes for individual samples. Table 6, Section 9, presents the analytical results of this sampling. These samples should present a representative indication of area formaldehyde concentrations within the plant during the time the samples were taken.

The production unit area samples (4 locations; 13 samples) range from below detectable limits (0.05 ppm) to greater than 3.63 ppm. The highest concentration was found on the ground floor near the primary reactor. None of the other samples in this area were as high as 1.0 ppm.

Two locations were sampled in the formaldehyde storage area. Analytical results show concentrations ranging from 0 17 to 0 35 ppm with average concentrations of 0.19 and 0.28 ppm. These levels are less than 10% of the OSHA PEL and indicate a well-controlled area

10.1.8 General Conclusion on Formaldehyde Exposure

The following general conclusions can be supported by the data collected

- Supervisors' chief operators' and unit operators' exposure to formaldehyde was nonexcessive during the survey and is probably nonexcessive at all times during normal operations.
- Unit operator exposures during potentially excessive short-term exposures, such as during truck loading and absorber sample withdrawal and analysis, were found to be non-excessive.
- The potential exists for excessive short- and long-term exposure maintenance workers and of service operators Personal protective equipment worn during maintenance activities should provide adequate control.

10.2 METHANOL EXPOSURE

10.2.1 Production Supervisor Long-Term Exposure

Two consecutive personal samples were taken for the production supervisor on each of two separate day shifts. One of the four sample tubes had breakthrough in the backup section of the tube, indicating that all of the methanol may not have been captured. This concentration, greater than 10.57 ppm, is still far below the OSHA limits. The remaining tubes were below laboratory detectable limits (0.3 ppm). TWA concentrations were below 1 ppm, less than 0.5% of the OSHA TWA PEL of 200 ppm and indicating a nonexcessive exposure. Results are presented in Table 4, Section 9.

10.2.2 Chief Operator Long-Term Exposure

Two consecutive personal samples were taken for a chief operator during a single day shift resulting in a TWA exposure of 0.32 ppm, which is nonexcessive when compared to the OSHA TWA PEL. Such a low result could have been expected based on the limited activity of this worker outside the control room.

10.2.3 Unit Operator Long-Term Exposure

Two consecutive personal samples were worn by unit operators during each of four different shifts (see Table 4). Total sampling periods were 4.6, 6.2, 6.8, and 7.0 hours. The latter three sampling periods should give representative TWA methanol exposures for the unit operators during these shifts. The initial sampling period (4 6 hours) is short of the necessary six hours because the second sample tube became disconnected from the sampling pump tube and had to be voided The replacement tube was started 118 minutes after the end of the sampling period for the first tube and only sampled for 111 minutes. As a result, this set of samples does not adequately represent the 8-hour shift.

One of the six remaining sample tubes had excessive breakthrough into the backup section (backup section contained more than 25% of the material found in the front section). As a result, this value (2.02 ppm) should be considered a minimum value. TWA results for the three sets of samples range from below detectable limits to greater than 1.28 ppm and indicate a nonexcessive long-term shift exposure situation (less than 1% of the OSHA TWA PEL) for the unit operator

Two sets of area samples were taken in the control building during two different shifts to determine the methanol vapor exposure within the building Results can be found in Table 7, Section 9. The exposure was expected to be low, even with methanol analysis being performed within the building. Sample No. 43 had excessive breakthrough into the backup section. The TWA concentration for one set of samples was below detectable limits, and for the other it was 0 55 ppm. This indicates a low methanol vapor exposure within the control building, contributing minimally to the operator's long-term shift exposure.

10.2 4 Maintenance Personnel Long-Term Exposure

The survey team was unable to take any personal samples on maintenance workers or service operators since none were working in the area at the time of the methanol survey. It is expected that most exposures of maintenance personnel would be nonexcessive. If workers would be involved in a project with a potential high methanol vapor exposure, they would wear adequate respiratory protection, which would be considered adequate exposure control.

10.2 5 Methanol Unloading

Three area samples were taken at the methanol unloading site. Results can be found in Table 7, Section 9. These samples were taken to evaluate the exposure potential during unloading, and to relate this exposure potential to the operator's long-term exposure, if high.

One (tube 44) of the three samples had excessive breakthrough into the backup section and thus, the listed value should be considered a minimum value. The average area concentration during the sampling periods at the methanol unloading period was greater than 3.11 ppm, which is approximately 1.5% of the OSHA TWA permissible exposure limit for long-term exposure. There is no OSHA short-term exposure limit for methanol As a result of these very low levels, it can be concluded that methanol unloading is not a significant source of methanol exposure From this conclusion, it follows that the truck driver who completes most of the work is also not overexposed to methanol since he spends most of his time away from the unloading area.

10 2 6 Methanol Area Sampling

In addition to the area samples already discussed (control room and methanol unloading), seven other areas were sampled during the survey. Five areas were sampled for an 8-hour shift and the remaining two for a 4-hour period. Two sample tubes were placed in series in three locations to avoid breakthrough problems Analytical results are presented in Table 7, Section 9. The individual samples ranged from below detectable limits (0.3 ppm) to >13.70 ppm and the TWA of two consecutive samples ranged from below detectable limits to >7.65. All samples indicate low levels of methanol in all areas, generally below 5% of the OSHA long-term TWA

10 2.7 General Conclusions on Methanol Exposure

The following general conclusions can be made about methanol exposure potential at this plant:

- All workers are probably not overexposed to methanol on either a short- or long-term basis.
- The truck driver who delivers methanol to the plant is probably not overexposed to methanol on a either short- or long-term basis.
- Area methanol concentrations are well below the OSHA TWA PEL standard of 200 ppm.
- Maintenance workers should not be overexposed to methanol if they use personal protective equipment during activities where there is an overexposure potential.

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. Two single mechanical seal centrifugal pumps with fluid return lines were sampled for formaldehyde during the survey. Concentrations inside the sample volume were 19 and 125 ppm, with the lowest concentration at the formaldehyde agitation and loading pump and the highest at the absorber bottoms pump. The first pump (formaldehyde agitation and loading pump) was in an open area and appeared to have no paraformaldehyde deposits. The absorber bottom pump was enclosed in an insulating box and was not visually inspected. The sampling results indicate that a small leak or paraformaldehyde deposit may have occurred in the pump housing, affecting the sample.

Analytical results for mass released per day for each pump sampled are summarized in Table 9. These results assume that the concentration released was constant within the volume and that the leak rate from the seal was constant. The samples indicate low release rate of formaldehyde from these pumps.

TABLE 9. MASS LOADINGS RELEASED FROM ENGINEERING CONTROLS

Description	Tube no.	Mass, µg/tube	Sampling time, min	Daily release rate, g/d
Formaldehyde				
Absorber bottom pump	1929	765	51	2.2×10^{-2}
	127	574	31	2.7×10^{-2}
HCHO agitation/loading pump	1862	114 8	51	3.2×10^{-3}
	85	64.5	28	3.3×10^{-3}
Methanol				
Methanol supply pump	32	168.33	111	2.2×10^{-3}
	42	115.78	118	1.4×10^{-3}

Data in Table 6 show that the measured concentrations of formaldehyde at the laboratory hood varied from 0.5 to 2.6 ppm, with an average of 1.5 ppm. All of these levels are well below the OSHA HCHO STEL of 5 ppm. Considering the high exposure which would be likely to occur if the formaldehyde samples were not handled inside of the laboratory hood, it is concluded that the hood is effective controlling emissions to acceptable levels. The effectiveness in further demonstrated by the fact that the formaldehyde levels in the other parts of the unit building only averaged 0.39 ppm, showing that the hood was successful in confirming formaldehyde contamination inside of it to that part of the building.

The formaldehyde concentrations in the area surrounding the reactors averaged less than 0.92 ppm on the first floor and 0.07 on the second floor. These values indicate that the process is sufficiently tight that excessive exposures would not be expected often in this area, although one of the seven samples did have a concentration of 3.63 ppm, which exceeds the OSHA HCHO TWA This is not a serious problem, however, because workers spend very little time in this area.

The formaldehyde concentration in the absorber area were measured to have an average value of 0.31 ppm, which is one-tenth of the OSHA HCHO TWA The burning of gas exiting from the absorber in the afterburner combined with its discharge high above ground level appears to be effective in controlling the ambient concentration of formaldehyde near the absorber.

The formaldehyde levels in the formaldehyde storage area were low during this survey, averaging less than 0.3 ppm The lack of controls on the tank vents seems to not cause significant exposure.

The concentrations of formaldehyde at the track loading station averaged below 0.40 ppm, with one value measured at 1.55 ppm. Even this highest level is well within the accepted OSHA limits. The ventilation duct appeared to be sufficiently effective during the June 1983 visit to control the concentrations in the area to acceptable levels.

10.3.2 Methanol Source Sampling

Table 8 in Section 9 presents the analytical results of the methanol source samples. Table 9 presents the mass loading release rate for the pump sampled. The single mechanical seal centrifugal pump appears to contribute very slightly to the general area concentration

The concentration of methanol in the methanol unloading area averaged just over 3 ppm during the October 1982 visit. This is far below the OSHA MeOH TWA of 200 ppm. The use of the natural suction on the methanol truck during its unloading appears to be effective in preventing a large release of methanol.

The methanol concentrations in the methanol storage area averaged over 1 ppm, a very acceptable level. The use of exterior level indicators to reduce the number of times the tanks must be opened probably is helpful in keeping this level down Samples taken near the circulation pump in the absorber area, which averaged near 0.8 ppm are quite low, indicating that the single mechanical seals with the methanol loop to help lubricate and flush the seal face is effective in containing the methanol being pumped.

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

APPENDIX A

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%), dimethylformamide, and hydrochloric acid were Fisher Certified ACS grades. Acetonitrile was Burdick & Jackson distilled in glass. Silica gel was from Aldrich (Catalog No. 2[illegible], 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 95 °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 50 °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.

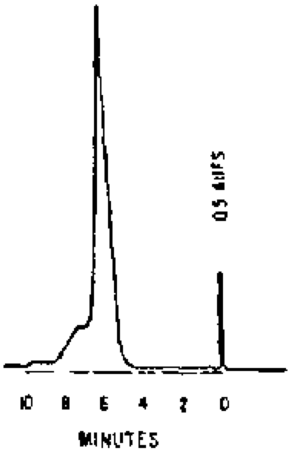

Figure 1. HPLC chromatogram for injection of 4.6 μg of formaldehyde-2,4-dinitrophenylhydrazone (equivalent to 1.06 ppm formaldehyde in air, for a 20-L air sample).

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.

Tubes prepared as described here were found to have a pressure drop of 7.5 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 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

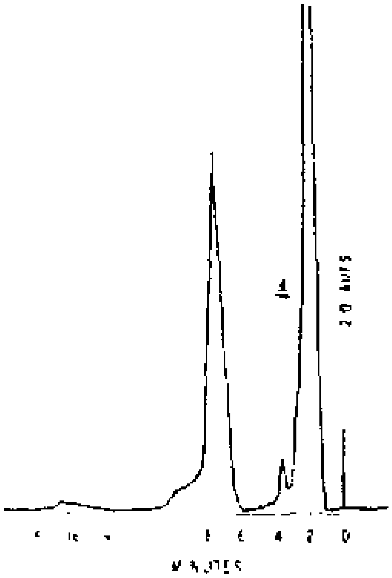

Figure 2. HPLC chromatogram for injection of sample resulting from collection of 122 μg of formaldehyde (4.96 ppm for a 20 L sample) on a 2,4-DNPH coated silica gel tube, as described in the Experimental section.

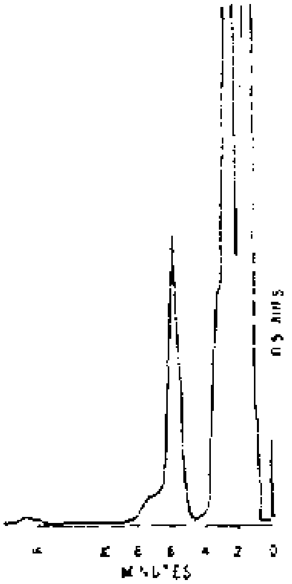

Figure 3. HPLC chromatogram for a field sample at a location where formaldehyde is used as a raw material. The sample was determined to represent 0.65 ppm formaldehyde in air.

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 (7-11) 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 (17) 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, 7, 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 0.02 (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 ~0.06 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 105 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.[illegible]	1.4
4	2.4	1.4
	$\bar{X}$ = 2.2, σ = 0.3	$\bar{X}$ = 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	0.85	1.76	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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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 ($\overline{CV}_T$)	0.073
Procedure	Adsorption on silica gel, desorption with water, GC	Validation Date	1/27/75

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 25-900 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 6 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. <u>Apparatus</u>

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate. (Reference 11.3)

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. <u>Reagents</u>

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 the same 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 of variations of FID response.

10 Calculations

10.1 Read the weights, in mg, corresponding to each peak area (and 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

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

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)