114-156

DETAILED INDUSTRIAL HYGIENE SURVEY
FORMALDEHYDE PRODUCTION

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GLOSSARY OF TERMS

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

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

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

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

SECTION 1

INTRODUCTION

The following detailed industrial hygiene survey report describes a four-day survey conducted at the Georgia-Pacific formaldehyde production plant located in Albany, Oregon. This plant used a metal oxide catalyst to convert methanol to formaldehyde at a rated capacity of 120 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 survey described in this report was carried out by Glen Barrett, (GEOMET Technologies) CIH, William McKinnery, Jr. (NIOSH) CIH, PE, David Dunn, and Dennis Gault (Monsanto Research Corporation), on July 19-23, 1982. Personnel contacted during the visit were Donald Olsen, CIH, corporate manager, industrial hygiene for Georgia-Pacific (GP), Greg Gregory, Albany plant manager, John Hillstrom, production superintendent, Thomas Moehl, quality control supervisor, and James Rouse, maintenance supervisor. Four operators under Mr. Hillstrom's supervision and two maintenance workers under Mr. Rouse's supervision were sampled for formaldehyde and methanol during the four-day survey. Mr. Olsen observed and noted all sampling operations during the survey.

1.2 SUMMARY OF ACTIVITY

The survey team met with plant personnel and Mr Olsen to discuss the purpose of the survey, desired results, activities to achieve these results, and the report that would result from this survey. Requests for cooperation with the survey team were made during the meeting and accepted by the plant. A short walk-through of the plant was conducted to acquaint the survey team with the formaldehyde production area. A small area in the quality control laboratory was committed to the survey equipment and served as a base of operations. All equipment was checked out and calibrated prior to any further activity.

IH sampling began on the day shift, Tuesday, July 20, and continued through the second shift, Thursday, July 22, sampling a total of six worker shifts (three day shifts; three second shifts). No sampling was conducted during the third shift due to logistics and similarity of operation on all shifts. Table 1 shows the total number and types of sampling conducted during the four-day survey. Personal exposure samples for formaldehyde and methanol were taken by sampling six individuals. Long term (over one hour) personal samples were taken to evaluate the general worker exposure. Short term (less than one hour) samples were taken to evaluate specific operations the worker conducted on a regular basis. Area samples were taken to determine the potential exposure of a worker in an area and to generally evaluate formaldehyde and methanol concentrations in the production and storage areas. Source samples were taken to evaluate the contribution of specific equipment to the overall area concentrations and to evaluate the control achieved by this equipment.

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

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

TABLE 1. SAMPLES COLLECTED DURING IH SURVEY AT THE GEORGIA PACIFIC FORMALDEHYDE PLANT IN ALBANY, OREGON, JULY 19-23, 1982

	Formaldehyde		
Type	Long-term	Short-term	Methanol
Personal	22	14	22
Area	21	-	24
Source	7	1	5
Total	50	15	51

SECTION 2

BACKGROUND

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

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

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

The objectives of the IH/CTA study are to:

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

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

The following sections briefly describe the objectives of this project.

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

- observing 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.

SECTION 3

DESCRIPTION OF PLANT

The Georgia-Pacific plant is located in an industrial park area approximately one mile north of Albany, Oregon, and began operations in 1973. The plant capacity is 120 x 10^6 lb/yr of 37 percent formaldehyde solution using an iron/molybdenum oxide catalyst Most of the formaldehyde solution is used on the site to manufacture phenol-formaldehyde and urea-formaldehyde resins. The remainder is shipped out by truck or rail to other customers, including other Georgia-Pacific resin plants.

The formaldehyde and resin production units are of open air construction. A plant site plan (Figure 1) shows the relationship of the formaldehyde production facility to the resin production facility and to the plant offices. Open air construction provides control of air contaminants through natural ventilation. The single control room used for both formaldehyde and resin production, the production laboratory facility, quality control laboratory, employee locker room, management offices, and warehouse are enclosed within a single building structure.

The plant is nonunionized and operates through four shifts, 7 days/week. The total plant employs approximately 40 employees, which include approximately 15 production operators.

The remaining employee job classifications are as follows:

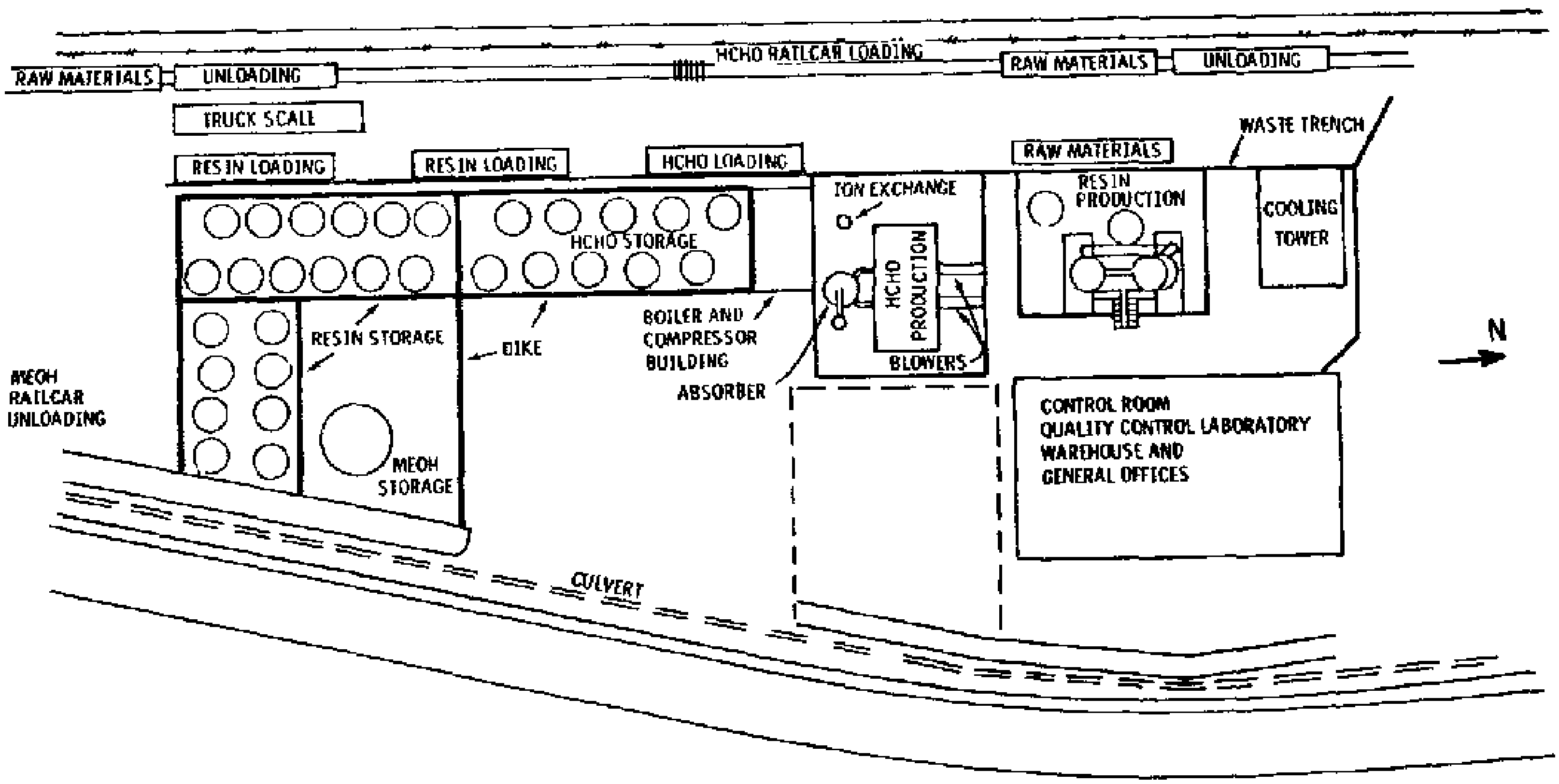

Figure 1. Georgia-Pacific Albany Chemical Plant.

- quality control laboratory supervisor

- management and clerical personnel

- maintenance superintendent

- maintenance workers

- laboratory personnel

The production operators are on rotating shifts, working every third day on formaldehyde production (one formaldehyde operator per shift) and elsewhere in the plant the other two days. Maintenance personnel work day shift, Monday through Friday, but are on 24-hour call for serious mechanical problems.

SECTION 4

PROCESS DESCRIPTION

Formaldehyde is manufactured by oxidation of methanol using an iron/molybdenum oxide catalyst. The production process takes place in two identical parallel trains as shown in Figure 2. Figure 3 is a photograph of the formaldehyde production unit in Albany.

Methanol is unloaded from a rail car to a bulk storage tank and then is pumped to the vaporizer. Air is simultaneously drawn through a primary filter and combined with the methanol. The methanol-air mixture is vaporized and fed to the converter, which consists of vertical catalyst-filled tubes. Dowtherm $A^{®}$, a coolant, is pumped through the outside of the converter and removes the heat of oxidation from methanol conversion. Dowtherm vapor is condensed and recirculated to the Dowtherm separator, and then to the converter. Hot formaldehyde gas, produced in each converter tube, is fed to the aftercooler. Cooled gas from the two parallel aftercoolers is united at the base of a single atmospheric absorber column. Liquid effluent from the absorber, containing 50-51 percent formaldehyde by weight, is stored in storage tanks. Gas emitted from the top of the absorber column, consisting mostly of nitrogen and oxygen, passes through a demister and is recycled to the methanol vaporizer through the compressor. An oxygen analyzer is used in-line to control the oxygen content of the air feeding the vaporizer to reduce the explosion hazard. The entire process has not been modified since initial startup in 1973.

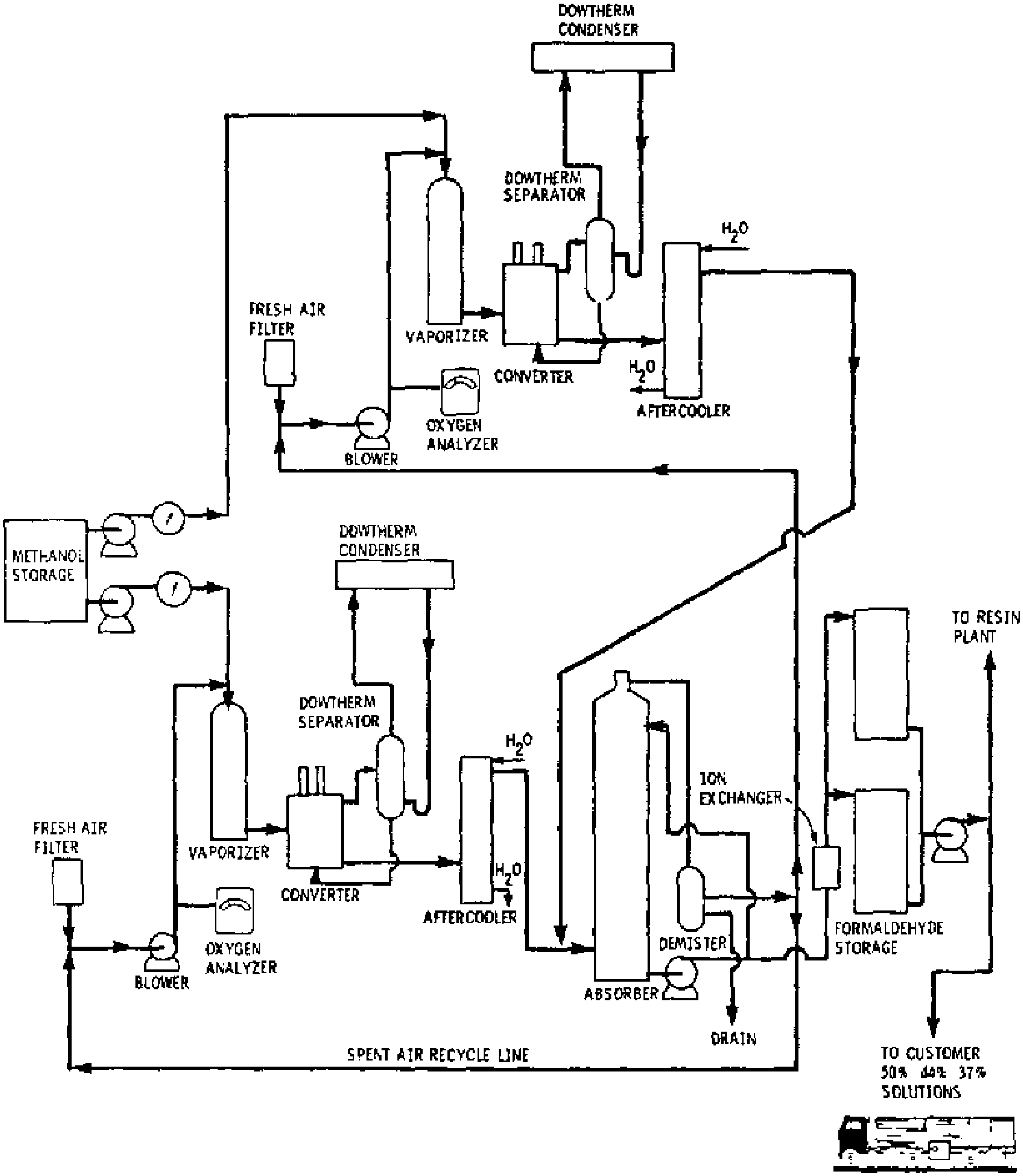

Figure 2. Process flow diagram for the Georgia Pacific formaldehyde plant in Albany, Oregon.

Figure 3. Albany, Oregon, formaldehyde production unit

SECTION 5

DESCRIPTION OF PROGRAMS

5.1 INDUSTRIAL HYGIENE AND SAFETY

The corporate and divisional offices in Portland, Oregon provide safety and health program guidelines to the plant. These guidelines can be modified by individual plants to meet specific needs. Examples are the divisional confined space entry procedure (Appendix A) and the equivalent modified plant procedure (Appendix B).

Each plant employee receives a Chemical Division safety manual which contains sections dealing directly with an industrial hygiene program. These are "Chemical Substances," "Laboratory Safety," and "Medical and First Aid." The safety manual provides procedural guidelines for the division, but the exact administration of the safety and health program is at the discretion of each plant. If accident and illness experience is kept within acceptable guidelines, the plant may operate its own program. If plant experience creates questions, the corporate and division offices will provide more direct guidance to assist the plant in reducing accident frequency and severity rates.

Georgia-Pacific employs an industrial hygienist at the corporate level, Mr. Don Olsen, who provides industrial hygiene service for all the plants. Plant personnel assist with sampling programs recommended by Mr. Olsen.

The plant holds one general meeting per month, with management and supervisory personnel and designated operating personnel attending.

Safety is specifically included as a topic. Specific safety topics discussed are accidents and their prevention, unsafe practices, as well as other important safety subjects.

The plant manager and the plant superintendent conduct routine walk-through safety inspections, supplemented by safety inspections conducted by operating personnel. Additional safety inspections are conducted periodically by safety personnel from the Eugene, Oregon, Georgia-Pacific office, and the Corporate Safety office in Portland, Oregon.

Contingency plans are defined, and the plant has a written fire emergency plan. The Albany fire department has visited the plant to determine fire-fighting methods needed for particular fires that could occur. The emergency spill cleanup plan is now in the process of being updated

The plant has had no lost-time accidents since 1974 No employee has reported an illness due to inhalation of a hazardous airborne material during the plant's existence (since 1973) However, one employee developed a general sensitivity to solvents and other chemicals (not determined to be work-related) and was transferred to maintenance.

5 2 OCCUPATIONAL SAFETY AND HEALTH (OSH) TRAINING

All newly hired employees are taken through a 60 to 90-day probationary training period. The plant superintendent reviews the division safety manual with each new employee during this period. The employee is under direct supervision by an experienced operator or lead operator during the probationary period. The employee then generally advances from the lowest level of responsibility at the utility level (loader, cleanup, etc.) to operator. Employees are under supervision as they advance.

Operators rotate between the formaldehyde and resin facilities, working in the formaldehyde facility every third day.

Employee turnover at this plant is low. There have been twelve replacements since 1973 (two of these for maintenance) with the newest hire two years ago.

At least one employee on each shift is trained in cardiopulmonary resuscitation. Most employees are trained in first aid.

5.3 PERSONAL PROTECTIVE EQUIPMENT (PPE) AND SAFETY EQUIPMENT

Rain gear, face shields, gloves, helmets, safety glasses, disposable dust masks, and protective clothing are available as needed, or on request Safety shoes and respirators are provided. An MSA self-contained breathing apparatus is available in the control room. Several supplied-air respirators are available, and the plant compressed air is monitored and meets the criteria for breathing air.

An emergency eyewash and shower unit is located on the ground level of the production unit in the vicinity of the tank truck and rail car HCHO loading areas, and at the resin loading area which is near the formaldehyde loading area.

All employees are required to wear hard hats and safety glasses with side shields while working in production areas. Additional PPE is required for specific operations as follows:

<u>Formaldehyde Loading</u>

Half-face organic vapor cartridge respirator
Rubber gloves

Methanol Unloading
Half-face organic vapor cartridge respirator
Rubber gloves

Formaldehyde Solution Sample Withdrawal
Rubber gloves

Catalyst Removal from the Converter
Half-face respirator approved for nontoxic dust

Sample Removal of HCHO Gas from the Aftercooler Inlet
Half-face organic vapor cartridge respirator
Rubber gloves

Formaldehyde and Methanol Sample Lab Analysis
No additional PPE is worn

Formaldehyde Storage Tank Entry
Full protective suit
Boots
Gloves
Air-supplied respirator

Maintenance Formaldehyde Leak Repair
Gloves
Half-face organic vapor cartridge respirator for major leaks

The plant has a brief written respiratory protection program in the division safety manual.

5.4 MEDICAL PROGRAM

All employees are given pre-employment physical examinations which include a back X-ray, urinalysis, a medical history questionnaire, and a baseline audiometric test. Employees are not given periodic physical examinations or specialty examinations for specific hazardous exposures. However, annual audiometric examinations are made available by a mobile unit brought to the plant site.

Medical services are available from the Albany Hospital located two to three miles away from the plant.

SECTION 6

WORK PRACTICES

6.1 GENERAL PROCEDURES

6 1.1 Operators

Operators are responsible for operating the formaldehyde production process, unloading methanol from tank cars, loading formaldehyde into rail cars and trucks, sampling the process, and prevention and clean-up of spills. Operators also change the catalyst in tubes during shut-down periods.

The operators are on rotating shifts, working every third day on formaldehyde production and elsewhere in the plant the other two days. Each shift is 8 hours in duration. Lunches are eaten on-the-job, usually in the control/lab room where the operator spends approximately 30 percent of his working hours. He is required to patrol the process area every two hours to check for malfunctioning equipment or process leaks, and is responsible for reporting mechanical problems to the maintenance department and requesting immediate repairs for serious problems Minor maintenance may be performed by the operator.

6.1.2 Maintenance

Maintenance personnel, working day shifts, Monday through Friday, are responsible for maintenance of the entire facility, including the resin plant Specific maintenance requests are recorded by the unit operators on a board in the maintenance shop. Maintenance personnel keep a log on all maintenance to be performed during the day shift and may be called in at any time during the evening shifts to repair serious mechanical problems that require immediate attention. Lunches are eaten on-the-job, inside the control/lab room or shop.

6.2 METHANOL UNLOADING

Methanol is received and unloaded from rail tank cars, with approximately one tank car unloaded daily.

Prior to unloading the rail car, the operator withdraws a methanol sample from the car through the top hatch This procedure is described in more detail in Section 6.6. After sample withdrawal and analysis, he attaches a quick-connect flexible line to the tank car for bottom unloading to the methanol storage tank.

Air from the flexible line is bled out of the connect line at the methanol unloading pump. A small amount of methanol is purged into a bucket during this line bleeding This methanol is either back-fed into the line by suction or, if the quantity is very small, the operator manually dumps the methanol back in the rail car through the top hatch

The operator leaves the area for most of the remaining unloading period. At the end of this period, methanol remaining in the line is purged into a bucket with air. Once the line is bled, it is disconnected and the top hatch is closed and secured

6.3 METHANOL SAMPLING AND ANALYSIS

A methanol sample is removed from a rail car prior to methanol unloading. The operator opens the top hatch on the car and then dips an open jar into the methanol. The jar is fastened to the end of a long rod. After the jar is filled, it is covered and taken to the control lab room for analysis by injection into the gas chromatograph. In addition, a specific gravity test may be run on the sample to determine purity. The specific gravity test and the GC injection are usually performed by an operator or lead operator.

6.4 FORMALDEHYDE LOADING

6.4.1 Truck Tank Loading

Approximately two trucks are loaded with formaldehyde per day. It takes approximately 30 minutes to load a truck. The operator supervises the loading, which is performed by the truck driver who is not an employee of the plant. The truck driver initially opens the tank top hatch (Figure 4) and places the loading spout into the tank (Figure 5). The operator sets the required load for the tank on the automatic delivery control device (Figure 6) located at the loading area. He remains in the vicinity of the loading area for most of the loading period, often talking to the operator. On occasion, he may get involved in starting automatic delivery of resin to a truck a short distance away while formaldehyde loading is proceeding. The operator remains in the resin loading area for a very short time, either to start or stop automatic delivery of the resin. Consequently, it is not believed that exposure to formaldehyde vapors resulting from resin loading is of any significance, and it is not expected to add to the exposure resulting from formaldehyde loading.

After loading is complete, the truck driver removes a formaldehyde sample from the tank for analysis (Figures 7 and 8). Once the sample is analyzed by the operator and the concentration determined to meet specifications, the loading line is purged with air into the truck. The truck driver then removes the loading spout from the tank and transfers it over to the operator (Figure 9). Any residual formaldehyde, spilled out of the spout onto the truck or ground during this procedure, is hosed off by the operator. The

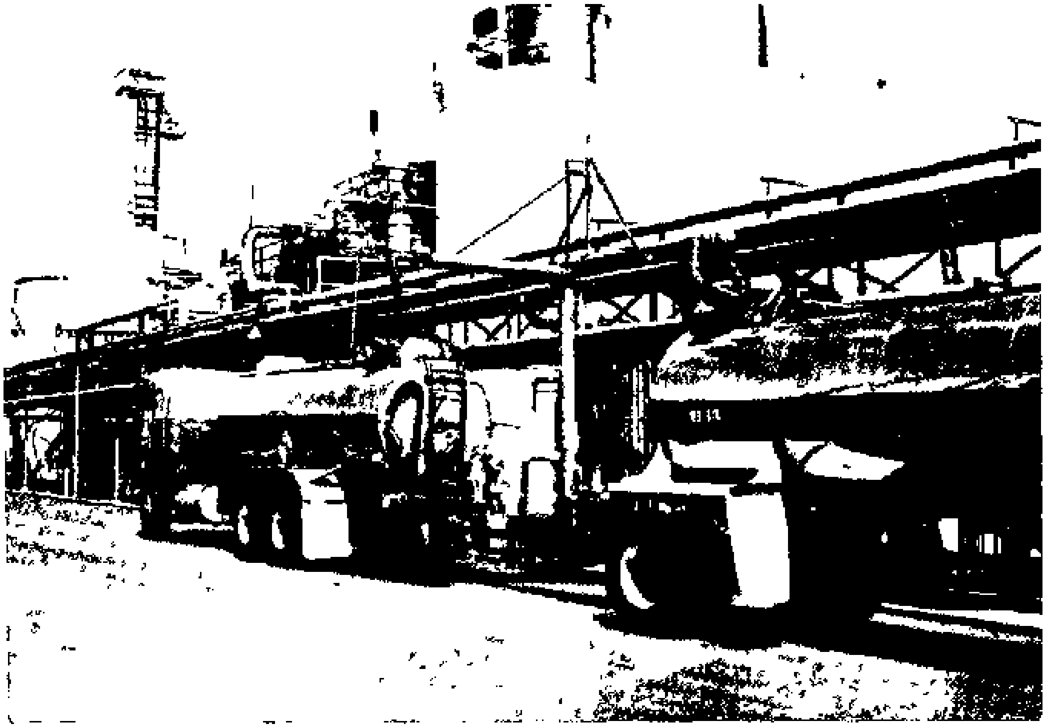

Figure 4 Loading a truck trailer - driver opens hatch of second tank as first tank is loaded.

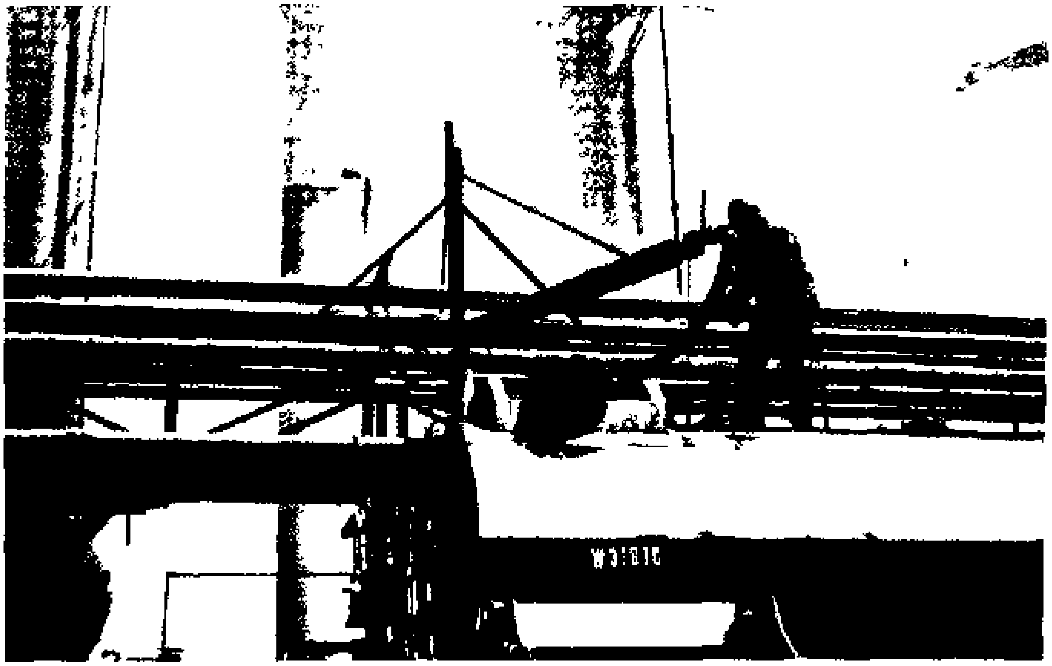

Figure 5. Loading a truck trailer - driver places loading spout in tank.

Figure 6 Loading a truck trailer - operator sets required weight load

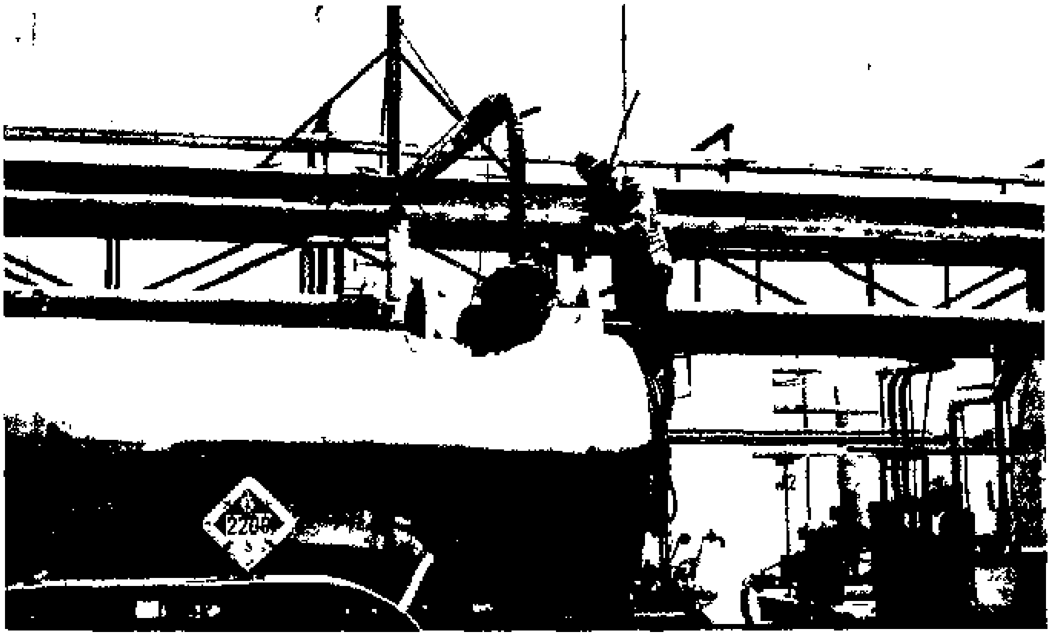

Figure 7. Sampling a truck trailer - driver prepares to sample with dip stick

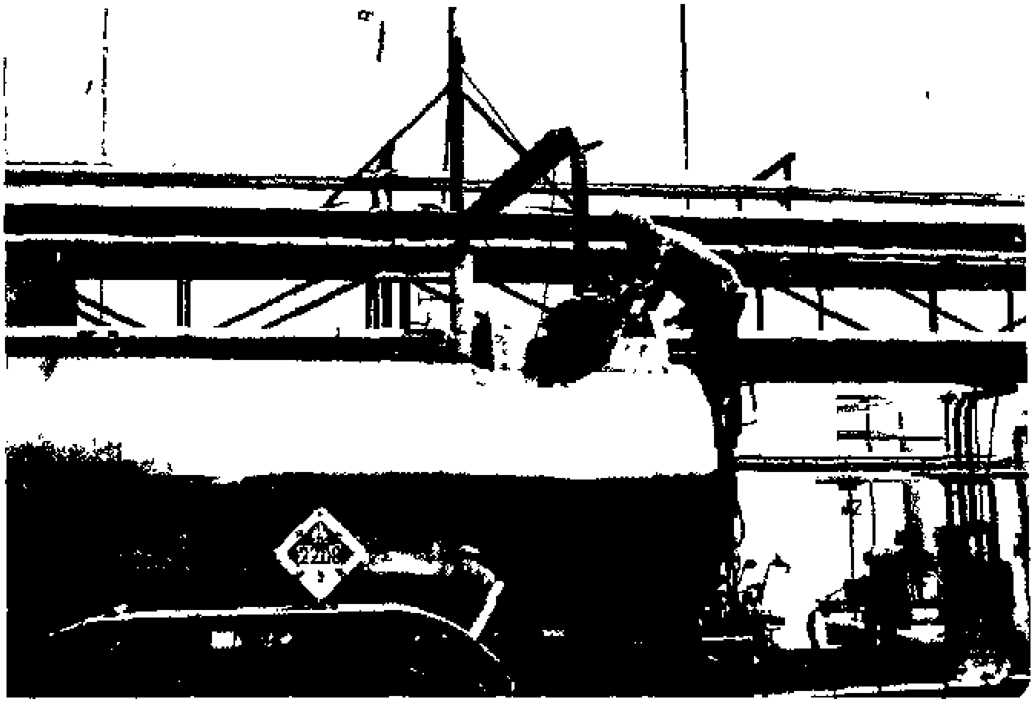

Figure 8   Sampling a truck trailer - driver sampling

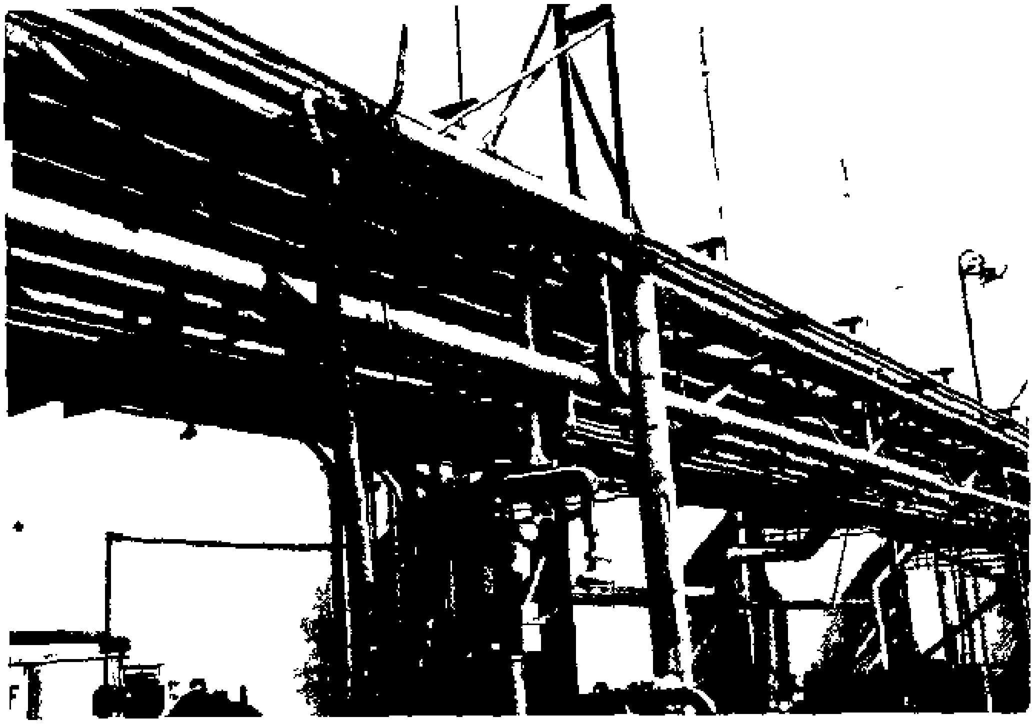

Figure 9   Loading spout in storage position

formaldehyde and water wash of the tank trucks go into a drainage sump that connects to the plant wastewater treatment plant.

6.4.2 Rail Car Loading

Approximately 16 rail cars are loaded per month. The operator performs all required duties. He initially opens the top hatch and then attaches a reinforced flexible line to the bottom of the tank car for bottom delivery. The operator starts automatic delivery by setting the load on the automatic delivery control device located at the loading area. The operator then usually leaves the area because loading usually takes 1.5 to 1.75 hours. Again, the operator may be involved in loading the resin.

After loading, the operator removes a formaldehyde sample through the top hatch for analysis. After analysis is completed and the sample concentration found within specifications, the delivery line is purged with air and removed from the rail car. No rail car loading occurred during this visit and hence there were no spills possible. If any did occur, they would also be washed into the drainage sump and then the waste treatment plant.

6.5 FORMALDEHYDE SOLUTION SAMPLE WITHDRAWAL AND ANALYSIS

The operator withdraws 50-51 percent formaldehyde solution from the absorber four times per shift by opening a ball valve and filling a 100-mL graduated cylinder (Figure 10). A catch basin, located below the sample point, is used to collect the purge of the sample line (Figure 11) and any excess solution or water rinse.

The open test tube is carried by the operator to the production control/lab room where a specific gravity test is performed after cooling the open graduated cylinder in the laboratory hood to 25°C (Figure 12). The liquid is stirred with a thermometer to aid in

Figure 10 Operator sampling the absorber at catch basin

Figure 11. Operator dumping purge into catch basin

Figure 12. Specific gravity test in the hood.

cooling, while the graduated cylinder is held under a cold water faucet. After the test, 30 mL of the sample is poured by the operator into an Erlenmeyer flask, which is placed in a cabinet controlled at 60°F where it is stored for further analyses. This entire procedure is carried out inside the hood reserved for this purpose. After the 30 mL sample is poured into the flask, the hood exhaust fan is turned on The remaining sample is rinsed out of the graduated cylinder in the sink next to the hood (Figure 13). A sink located within the lab hood is not used for this purpose. Waste water from both sinks drains into the plant's waste treatment pond

Thirty milliliters of each absorber sample taken over a 24-hour period is added to the Erlenmeyer flask that was previously placed in the cabinet. This conglomerate solution is analyzed once every third shift by the operator for percent formic acid, percent formaldehyde, and specific gravity. From these three analyses, the sample content is determined.

Figure 13. Process sample waste poured down unhooded drain with water flush.

For the percent formic acid determination test, the sample is automatically titrated (Figure 14) with sodium hydroxide. The entire procedure is performed outside the lab hood. In order to determine percent formaldehyde in a sample, the sample is titrated automatically with sodium sulfite. This is also performed outside the lab hood. The waste from both analyses is dumped down the sink outside of the lab hood. The specific gravity test is performed inside the lab hood.

Percent formic acid and formaldehyde analyses are also run on a single sample obtained from each rail car or truck tanker loaded with formaldehyde solution. Approximately 14 total rail car or truck tanker samples could be analyzed in a week. The truck tanker samples are obtained by the truck driver opening the top hatch on the tank and manually dipping a jar on the end of an

Figure 14. Automatic titration (out of hood) of process sample.

extended rod into the filled tank to obtain a sample. The truck driver then covers the jar and hands it to the operator who takes it to the control/lab room for analysis by another operator. Rail cars are sampled in the same manner by the operator.

Formaldehyde samples are drawn from storage tanks when the tanks are blended. Blending of product formaldehyde solution and water is done in two of the formaldehyde storage tanks prior to loading to adjust the solution to the proper concentration. Formaldehyde samples are drawn by the operator from the blended tanks. A jar is filled from a sample point on the lower wall of the tank. The jar is closed and taken to the control/lab room and analyzed for percent formaldehyde. The procedure is performed outside of the hood.

6.6 FORMALDEHYDE GAS SAMPLE WITHDRAWAL AND ANALYSIS

A formaldehyde gas sample is drawn by an operator or the quality control supervisor into a syringe through a sample valve in the aftercooler inlet. This sample is then injected by an operator or quality control supervisor into the gas chromatograph in the control/lab room and analyzed. This is usually done once every third shift, or more often, up to three-four times per shift, if process changes such as catalyst adjustment are involved.

SECTION 7

CONTROL STRATEGY

Several areas of the formaldehyde 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 railroad tank cars by the process operators who chock and ground the rail cars and post a sign on the rail siding to indicate that the tank car is being unloaded The unloading area is approximately 1,000 ft from the main production area.

During unloading, the operator opens the bolted tank car lid, removes a sample from the tank car (see Section 6), and leaves the lid partially open (two- to three-inch gap) to allow for air to displace the methanol drained from the tank car. This small gap does not present an exposure problem because the suction, created as the tank drains, draws air into the tank and prevents any escape of methanol vapors. Next, the operator removes the cap from the standard tank car discharge outlet (shown capped in Figure 15) and connects a quick-connect adapter to the outlet. Occasionally this cap holds a small volume of methanol to which the operator could be exposed through skin or eye contact or inhalaion This occurred once during the survey.

Figure 15. Tank car cap on discharge point.

A reinforced rubber flexible hose with quick-connect fittings and a neoprene rubber gasket for a tighter seal at each end (Figure 16) is attached to the installed adapter on the tank car and to the piping on site (Figure 17). Methanol is then pumped from the tank car through the hose and piping to the bulk methanol storage tank located about 400 feet away. An Ingersoll-Rand vertical in-line centrifugal pump fitted with a John Crane single mechanical seal is used. The seal uses a methanol loop from the pressure side of the pump to wet and lubricate the seal. A carbon rotary sealing and Teflon wedges are used to seal the pump shaft from leaking This particular pump did have a small methanol leak during operation (see Section 9). The methanol unloading pump is checked semi-annually and normal maintenance includes replacing the carbon rotary seal ring and possibly the Teflon wedges. A spare pump is available if a major overhaul is necessary.

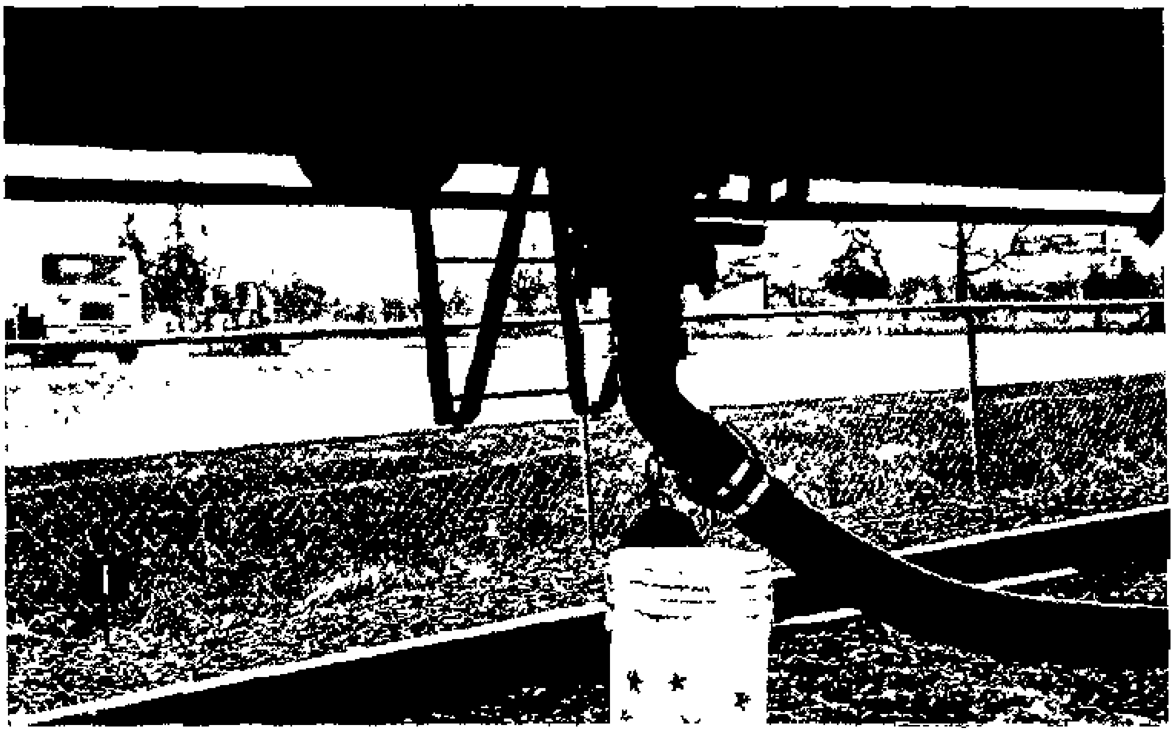

Figure 16. Methanol tank car with threaded adapter and quick connect line

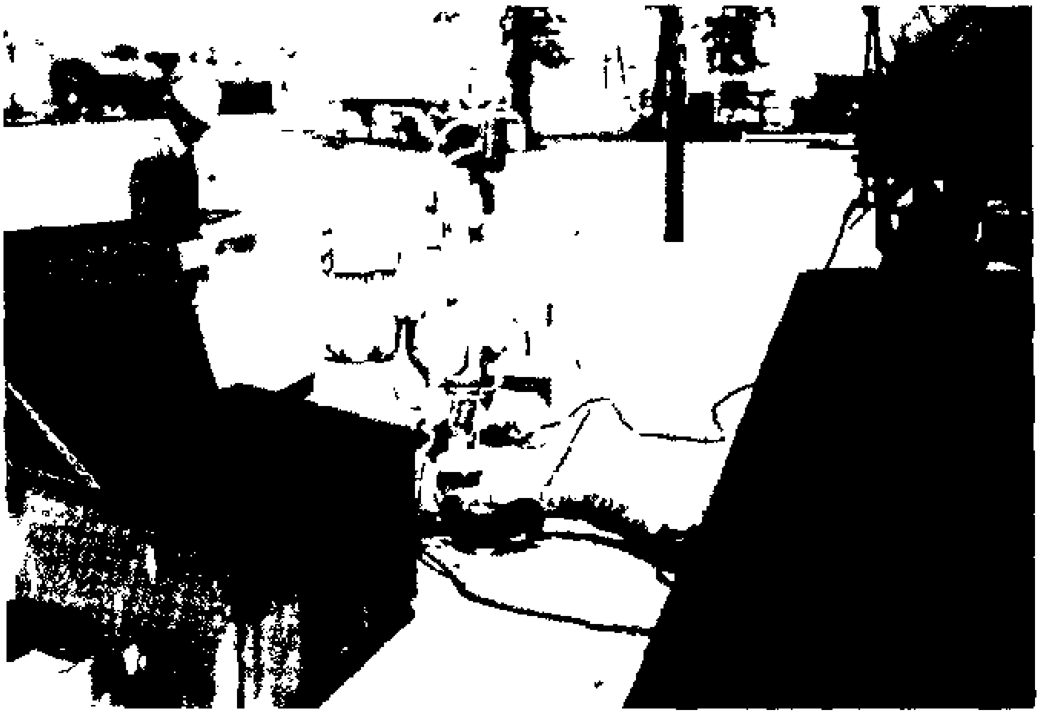

Figure 17. Methanol unloading line hooked up to permanent line and methanol unloading pump

The pump shown in Figure 18 is primed by gravity. The gravity feed from the tank car fills the pump with methanol while air from the pump and flexible line escapes through the bleed valve located on the pump discharge line. Any methanol that comes through the bleed valve is collected in a bucket by the operator and returned to the pumping system by suction. The pump has a screen shield around the housing to prevent worker injury from the spinning pump shaft. When the flexible hoses are not in use, caps are placed on the quick-connect ends to prevent inadvertent methanol leakage.

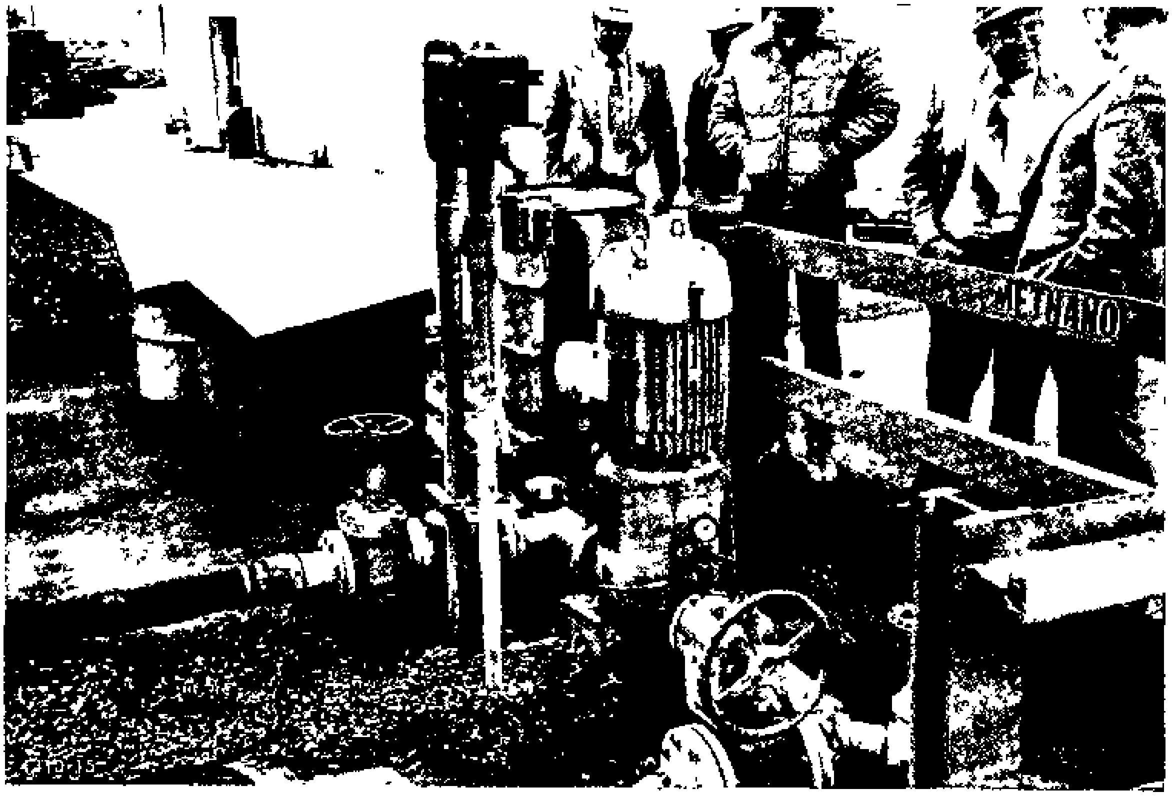

Figure 18 Ingersoll-Rand centrifugal methanol transfer pump with lubricating loop

7.2 METHANOL STORAGE AREA

Methanol is stored in a two-hundred-thousand-gallon storage tank approximately 400 feet from the unloading area and 500 feet from the production area. Methanol is delivered from the unloading area to the production area through underground pipe. The methanol level in the tank can be monitored by an external Shard and Juss level indicator.

As the methanol storage tank is filled, the discharged gases pass through a small condenser. Condensed methanol regurns to the storage tank. No estimate has been made on the amount of methanol recovered or released.

Methanol is pumped from the storage tank to the production area by a pair of Ingersoll-Rand centrifugal pumps that deliver approximately 20 gpm each. These pumps are similar to the pump used for methanol unloading except for the pumping rate (20 vs. 400 gpm). John Crane seals are used with recirculated methanol lubricating the seal faces. These pumps are equipped with an automatic shutdown feature that stops methanol from flowing to the production areas should an emergency occur. Shutdown is activated by low methanol flow, a large pressure drop across the reactor, or high oxygen levels Figures 19 and 20 show the methanol storage area and pumps.

The bulk storage areas are protected by dikes. A dike also separates the methanol storage area from the other bulk storage areas of the plant. The methanol tank is grounded and a permanently-mounted fire water jet is available within 75 feet of the tank.

7.3 CONVERTER AREA

The parallel tandem converters and supporting units are side-by-side in an open air structure as shown in Figure 21. Methanol and

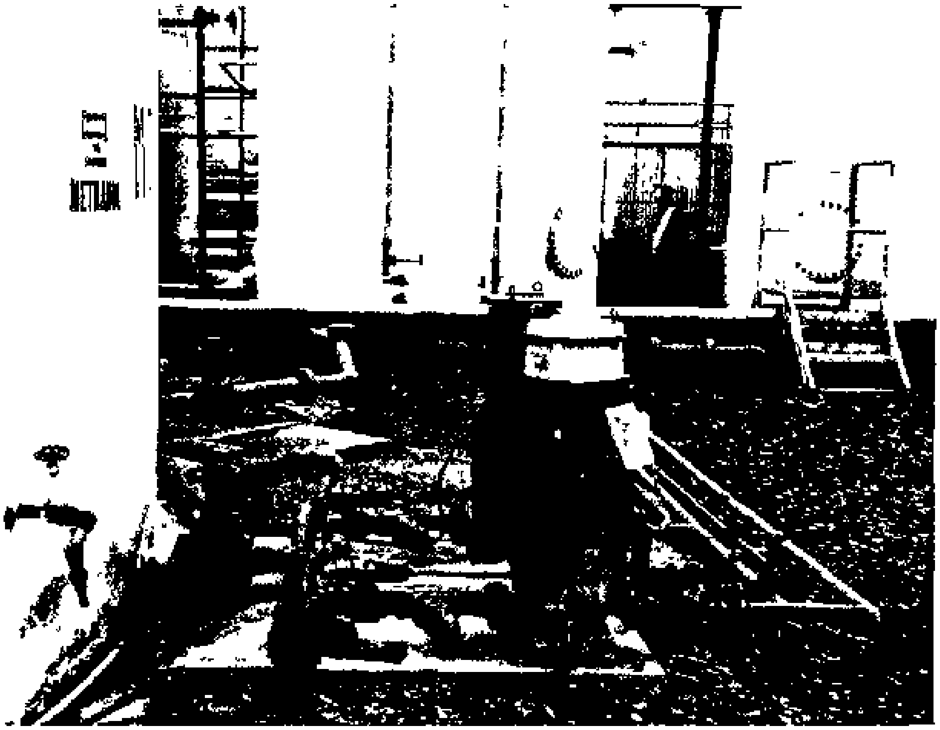

Figure 19 Diked storage tank and centrifugal methanol supply pump

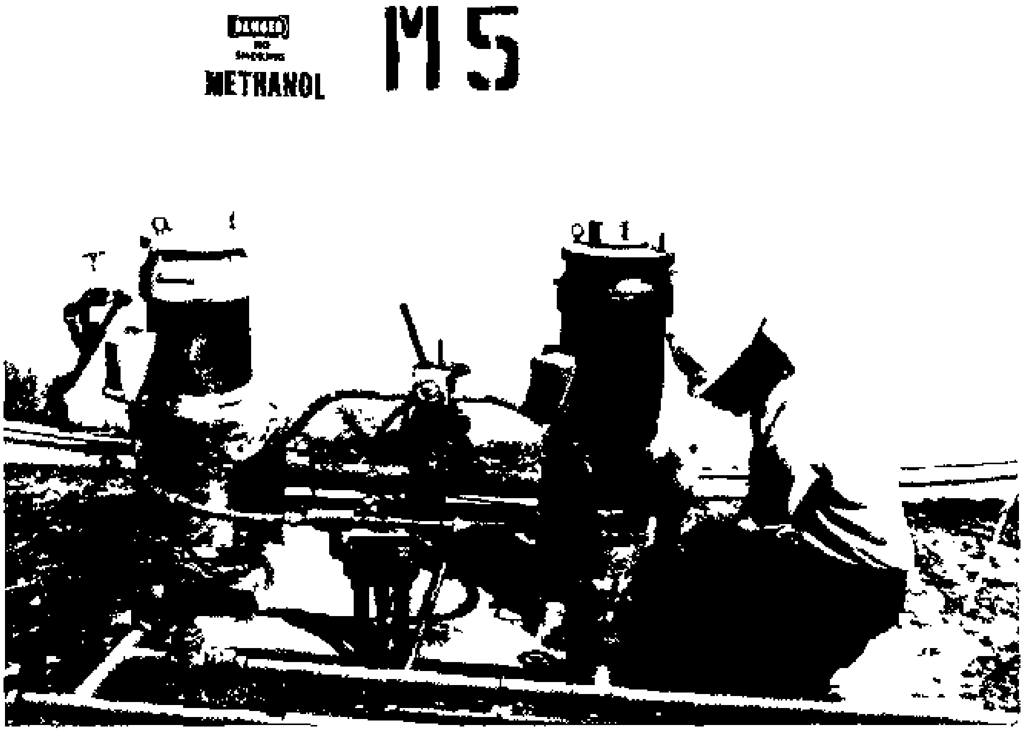

Figure 20 Methanol supply being prepared for source sampling

Figure 21. Production area; northern side. Converters on left and right of vertical vaporizers.

air are mixed, heated, and react in a closed system, preventing escape of reactants. Dowtherm A is used as a heat-transfer fluid for the converter temperature control and to produce steam for in-plant use. An oxygen monitor on the gas feed to the converter is used to maintain the oxygen levels outside of the methanol explosive limits (by controlling the amount of absorber gas recycle) and thus enhance process safety. Also, the converters have low- and high-pressure sensors designed to shut the system off during a malfunction, and have rupture disks with vent chimneys, such as the one shown in Figure 22, to reduce explosion damage should a converter over-pressurize. The product formaldehyde gas is sampled through a valve in the aftercooler inlet (Figure 23). A heated and insulated gas syringe is used to withdraw the sample which is injected directly into a gas chormatograph (see Section 6). During sampling, the operator uses a half-face organic vapor cartridge respirator for protection and safety shower and eyewash are located nearby on the first floor to treat any operatr in case of a spill or exposure.

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

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

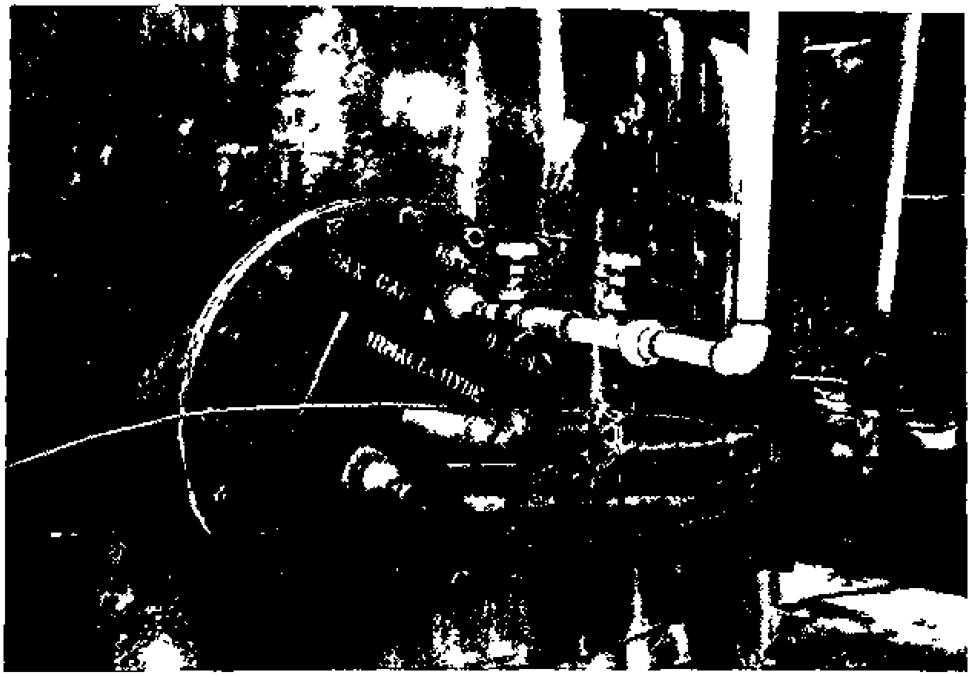

Figure 23. Formaldehyde storage tank manhole with steam lines attached.

The nature of the enclosed process makes additional controls in this area unnecessary. All valves are tightly packed to prevent leaks and appear well maintained Results of area sampling confirm the effectiveness of controls in the converter area.

7.4 ABSORBER

Hot product gas at about 150°C leaves the aftercoolers and enters the absorber where it is quenched with an aqueous formaldehyde solution The absorber shown in Figure 24 is a tray column.

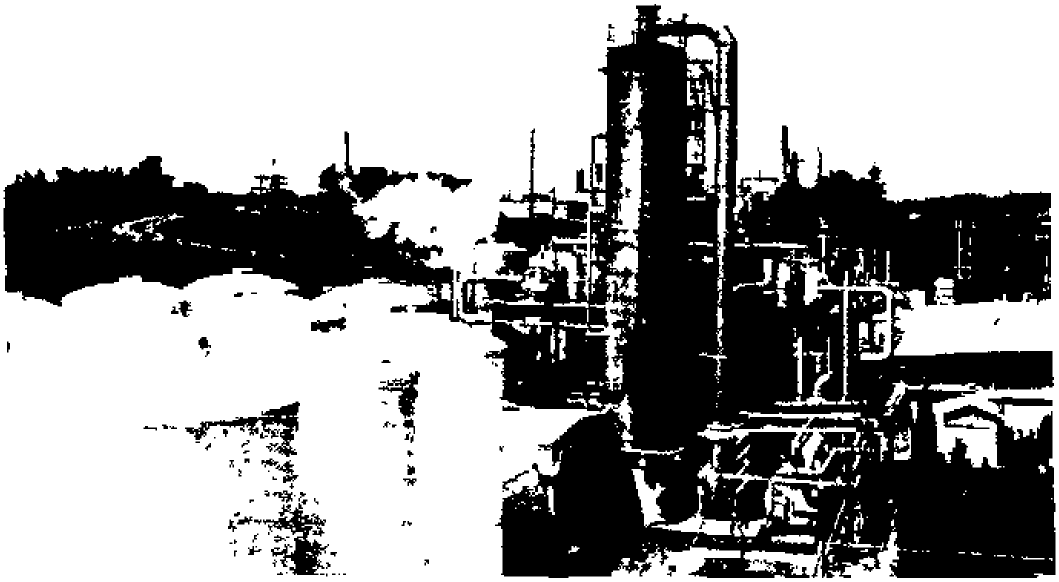

Figure 24. Left to right: storage area, absorber, production area. Lower right corner - maintenance workers installing shed.

All of the gas from the top of the absorber, mainly nitrogen and oxygen, is recycled through the recycle duct and demister seen to the right of the absorber in Figure 24 and used to adjust the percent oxygen in the converter feed.

A pair of Ingersoll-Rand centrifugal pumps with John Crane seals pump the formaldehyde solution from the bottom of the absorber.

A portion of this solution is recycled back to the absorber to capture the formaldehyde. The formaldehyde solution is used to lubricate the seals and steam is used in the pump glands to keep formaldehyde in solution and prevent paraformaldehyde formation. Figure 25 and Figure 26 show the seals and steam lines for one of the two pumps. Each pump can be used as a solution recycle pump or a product pump on an alternating basis.

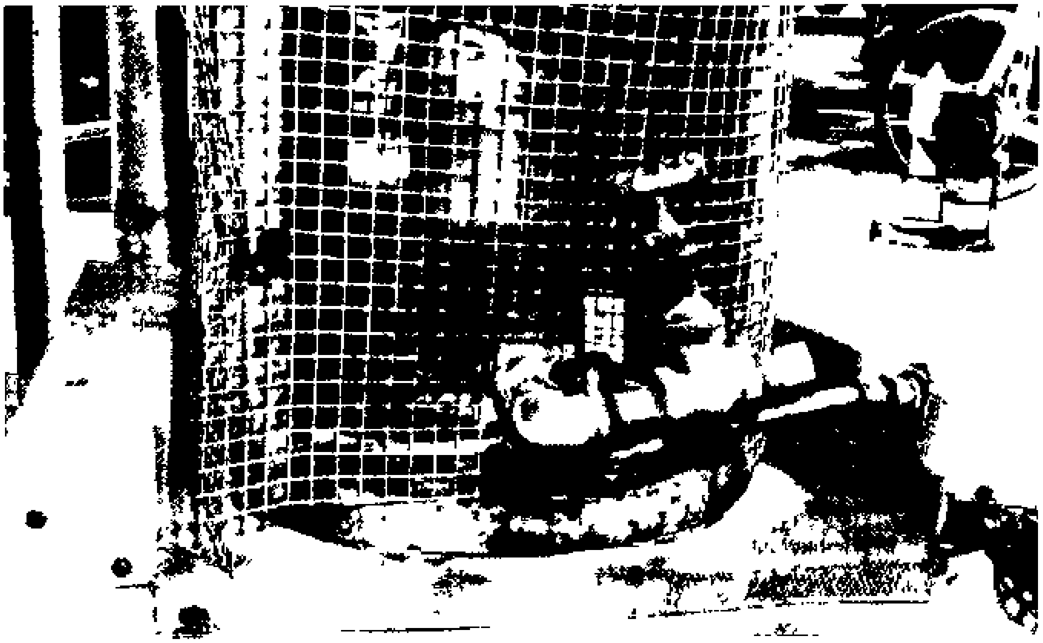

Figure 25. Steam lines and pump mechanical seal for formaldehyde pump on absorber.

Process sampling is conducted every two hours from the discharge side of the operating solution recycle pump (Figures 27, 28, and 29). Sampling lines can be purged directly into an open catch basin (Figure 30) that includes a water rinse that prevents manual dumping of the purge solution. The purge solution and water rinse drain into a small closed collection tank. When the collection tank is full, indicated by solution overflow into an adjacent open overflow bucket, the collection tank is closed off and air pressure is applied to force the solution into the absorber, preventing any

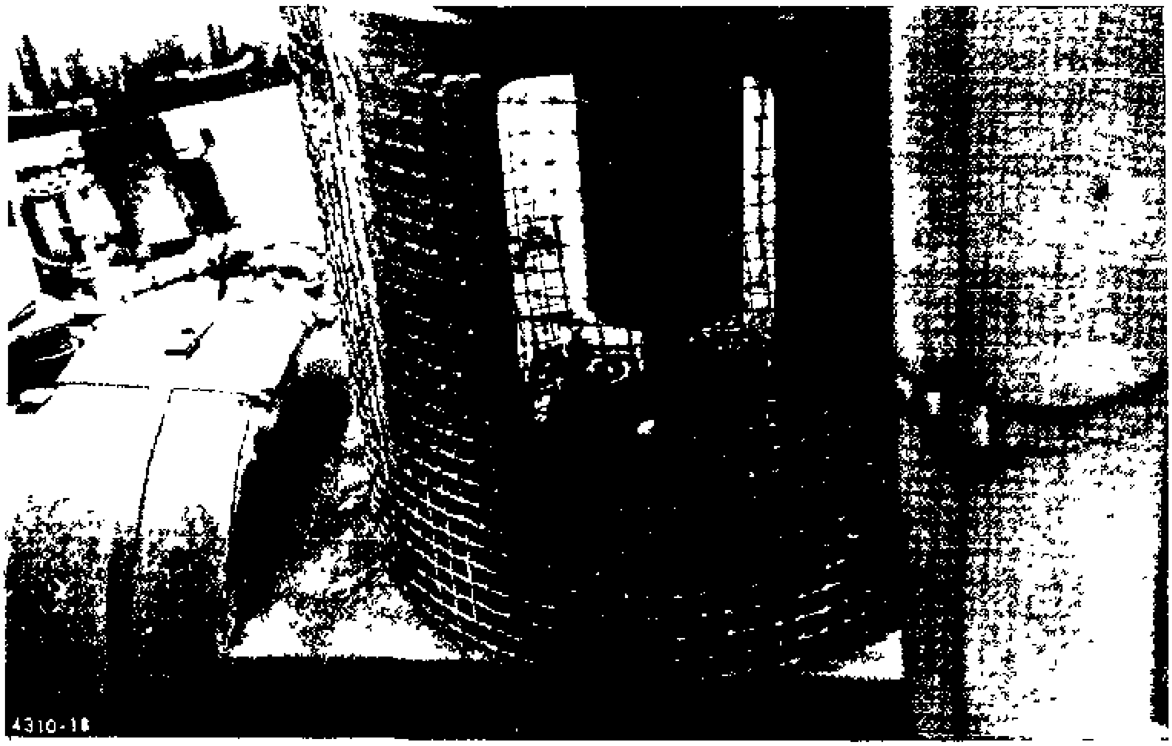

Figure 26 Centrifugal formaldehyde pump on absorber recycle with steam-heated mechanical seal

Figure 27 Front view of absorber sample point Holding tank is in foreground, absorber in background

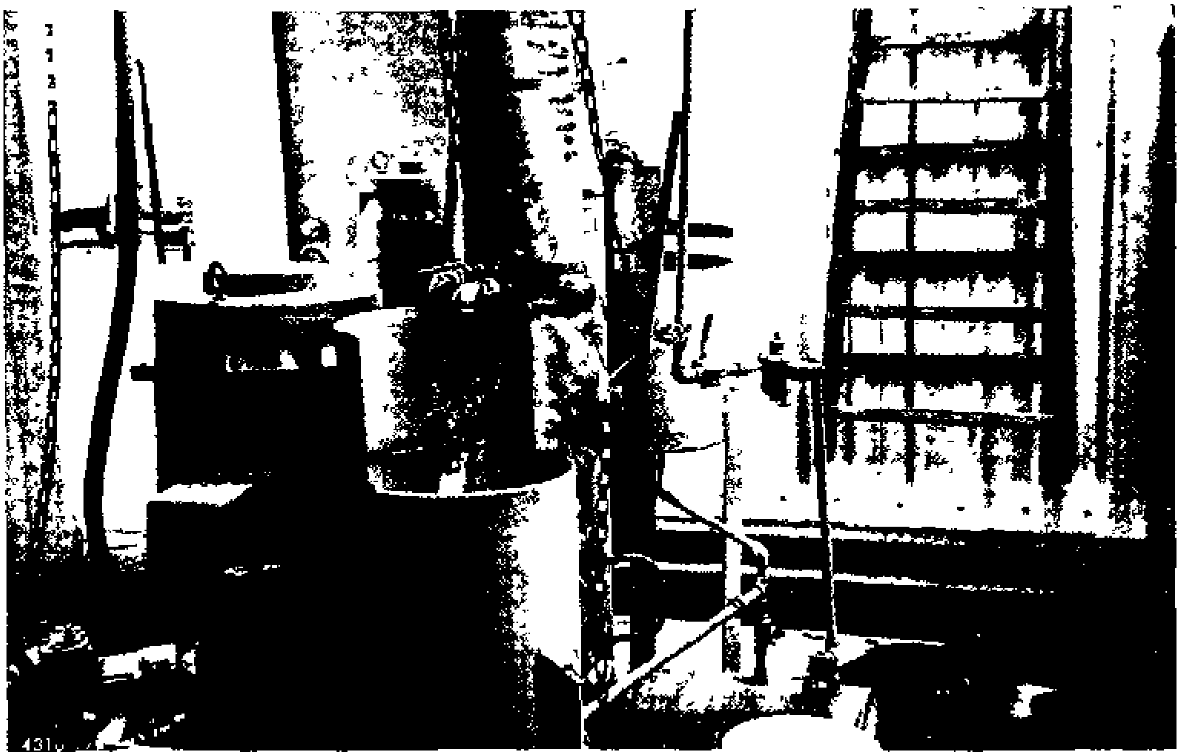

Figure 28. Side view of absorber sample point. Holding tank is below catch basin

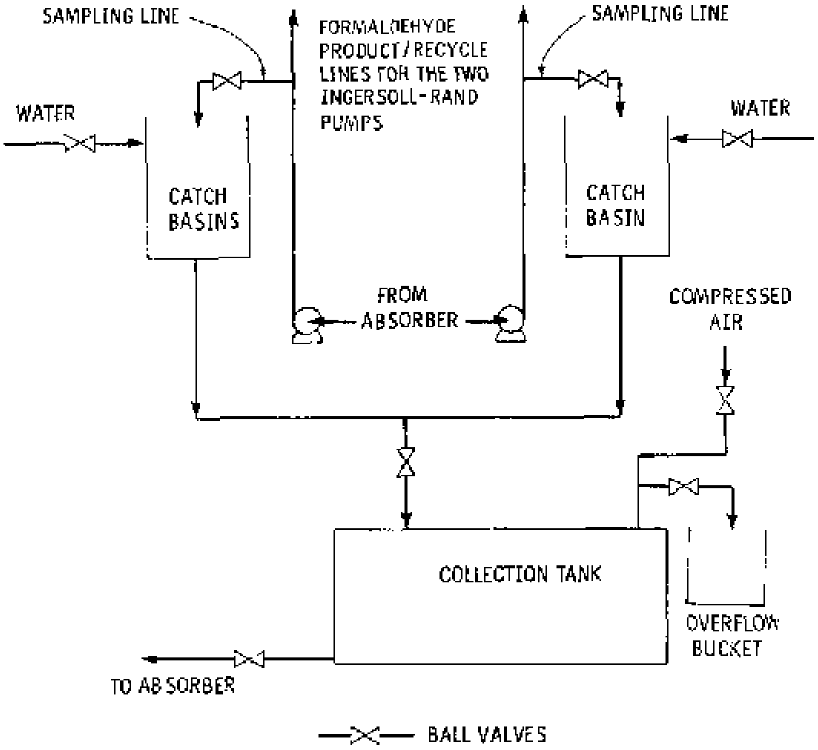

Figure 29. Schematic of process sampling/purge collection system.

Figure 30. Absorber sample point and catch basin.

secondary handling and operator exposure. A safety shower and eyewash are within 15 feet of the absorber sampling point.

7.5 FORMALDEHYDE STORAGE

Formaldehyde is stored in 10 storage tanks in a diked area approximately 100 feet from the production area and adjacent to the loading area. The location of this storage area can be seen in Figure 24

The formaldehyde storage tanks are vented through vents equipped with no controls This increases the exposure potential in this and adjacent areas.

7.6 FORMALDEHYDE LOADING

Centrifugal pumps similar to those used at the absorber are used to transfer the formaldehyde from the storage tanks via the interconnecting piping to the loading area All pumps are equipped with John Crane single mechanical seals that use recirculated formaldehyde for lubrication and steam glands to prevent paraformaldehyde formation.

Formaldehyde is loaded into tank trucks and railroad tank cars. Formaldehyde is loaded into the tank trucks using a top-loading, swivel-jointed, flexible loading spout shown in the storage position in Figure 31 and in use in Figure 32. As described earlier, the truck driver is responsible for loading the truck including inserting and removing the loading spout, while the operator supervises the operation An automatic delivery control device monitors the amount of solution delivered and shuts the flow off when the dialed load is delivered. This prevents spills and eliminates manual level checking by the driver and operator. Tank cars use the same delivery control but use a reinforced flexible hose to fill the tank car from the bottom.

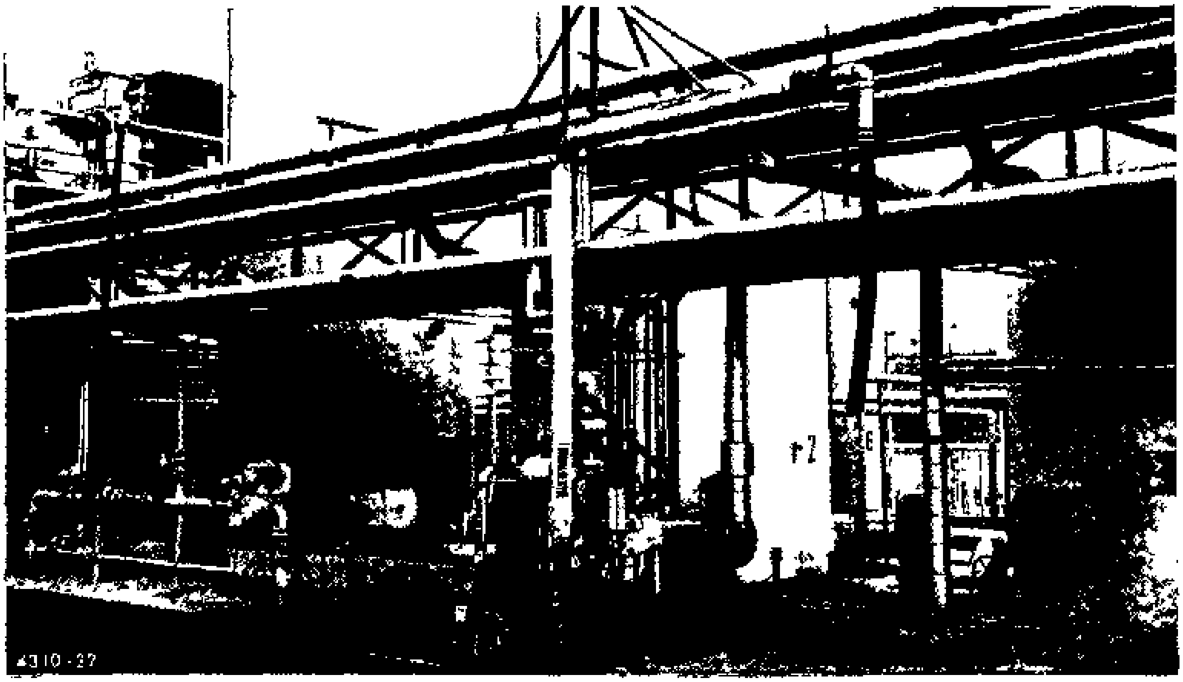

Figure 31 Formaldehyde tank truck loading area with swivel boom and flex-line loading spout and safety shower/eyewash station in background.

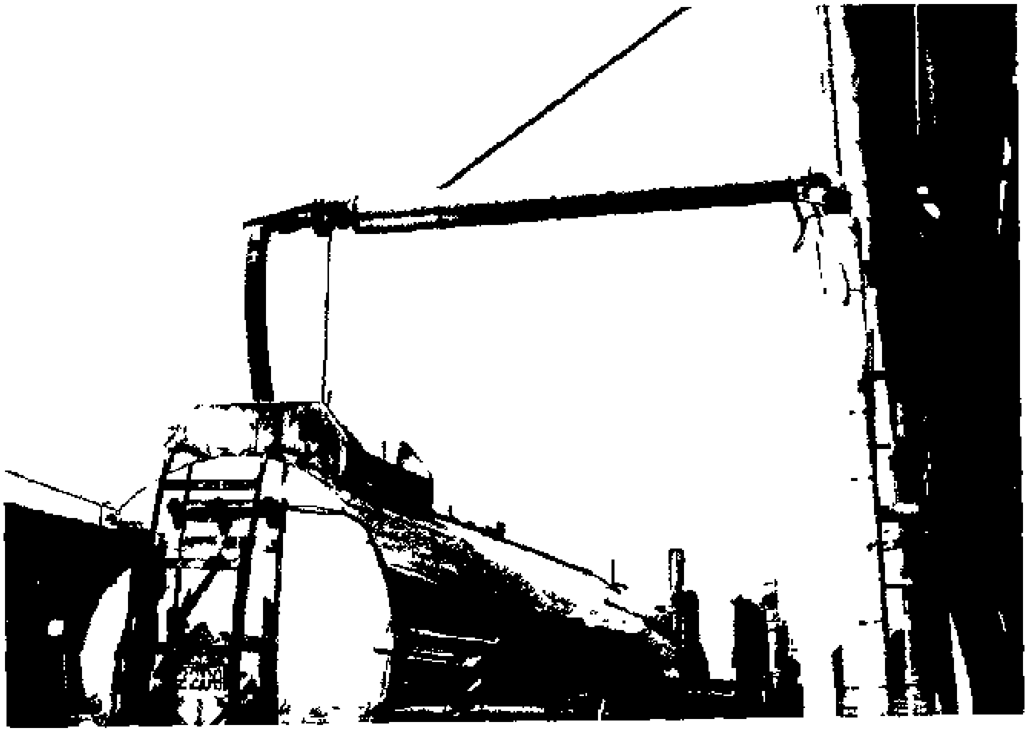

Figure 32. Formaldehyde loading boom in use.

7.7 CONTROL ROOM

Operators spend most of their time monitoring the plant production units from a single control room located in the rear of the main building. Critical operations can be monitored and controlled from this area and alarms alert the operators to problems. Storage tank levels can be monitored at an area in the warehouse adjacent to the control room.

Simple analyses on the samples collected from the processes are conducted in a small hood in the control room and vented through the roof The hood is located in an area that is easily accessible through the exterior doors. This reduces the time required to place the samples in the hood and minimizes escape of vapors from the samples brought into the control room A controlled temperature cabinet used for storage of formaldehyde samples is also available in the hood

Formaldehyde and methanol specific gravity tests are performed within the ventilated laboratory hood. Also located within the hood is a sink which conducts waste poured in it to the plant waste treatment pond.

Hood face velocity measurements were taken with an Alnor Jr. swinging vane anemometer. The following average face velocities were determined:

State of Hood	Average face velocity, fpm
Window fully open	114
Window pulled halfway down	172

With the window fully open, the average face velocity is considered adequate to control either formaldehyde or methanol vapors while performing specific gravity tests. A minimum average face velocity of 100 fpm is recommended to adequately control formaldehyde gas and methanol vapor Reducing the open face area of the hood by one-half, by pulling the window down, greatly increases the average face velocity to 172 fpm.

SECTION 8

SAMPLING AND ANALYSIS

Formaldehyde and methanol sampling was conducted during the five-day survey to determine time-weighted average (TWA) and short-term exposure levels (STEL) for personnel and areas associated with formaldehyde production at the Albany plant. Four formaldehyde process operators and two maintenance workers were sampled during at least one normal 8-hour shift to determine their average level of exposure to formaldehyde and methanol. The process operators and the quality control supervisor were also sampled during potentially high exposure activities for short-term exposure levels. Ten areas frequently attended by the formaldehyde process operators were sampled over an 8-hour shift to determine area concentration levels In addition, eight sources of potential emissions (e.g , pumps, seals, and agitators) were sampled to determine their contribution to the area concentration levels. In order to ensure that the samples represent 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 as shown in Figures 33 through 35. The concentration levels in the source samples were assumed to correspond to the amount of agent released by the source over the sampling period and expressed as the amount 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

Figure 33. Methanol supply pump being source sampled.

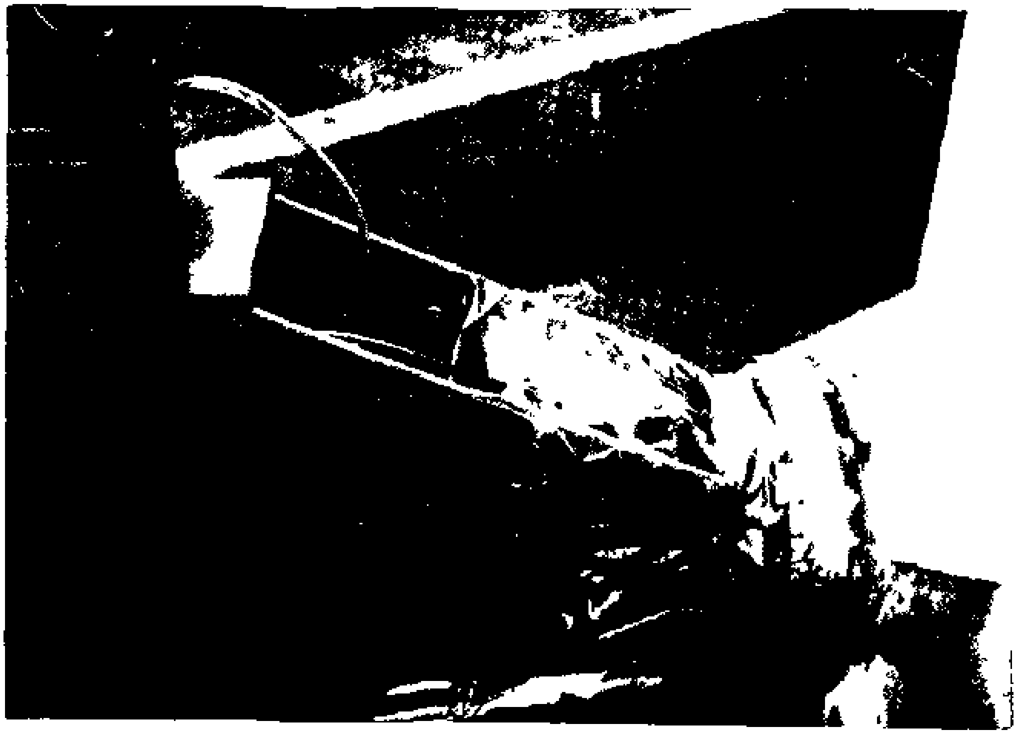

Figure 34. Side agitator on formaldehyde storage tank wrapped for source sampling.

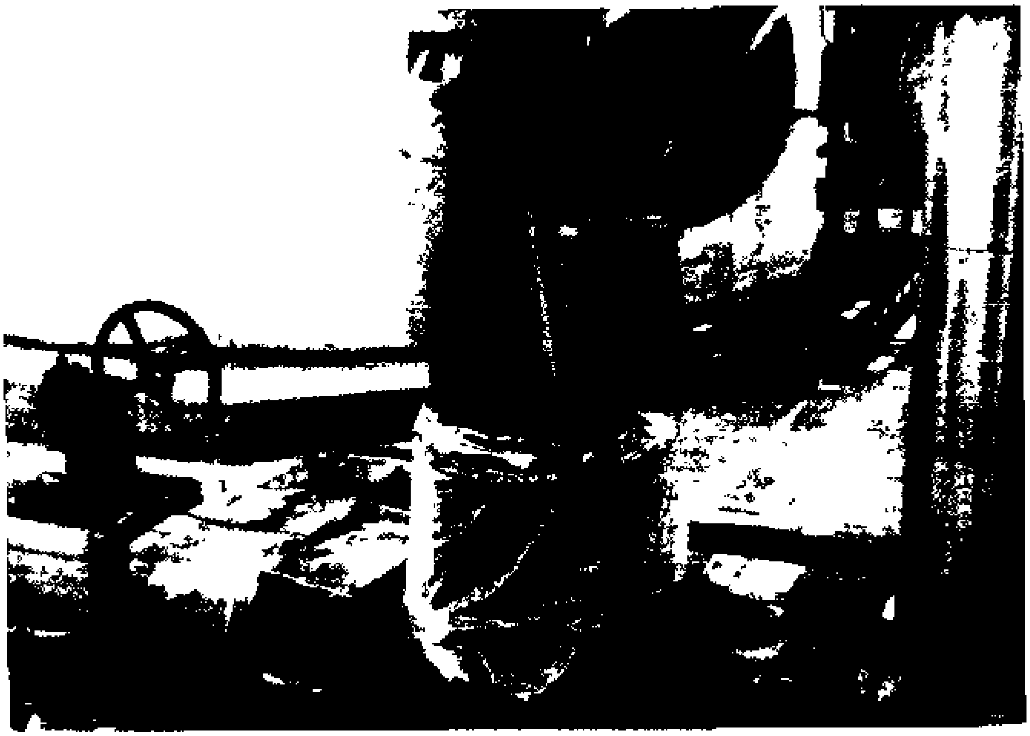

Figure 35. Loading pump wrapped for source sampling.

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 Long-term samples were generally comprised of two, approximately 240-minute long, consecutive sampling periods and were used to determine an eight-hour, time-weighted average according to the following formula

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

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 Most personal and area long-term samples were repeated on a second day to enhance the survey results and to evaluate results reproducibility.

Short-term samples were taken to evaluate significant short-term exposures, situations where peak exposures might be expected but not shown in the long-term samples. The short-term samples were also to indicate where controls may be 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 a 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 [Appendix C] and approved by the NIOSH project officer, Mr. W. N. McKinnery, Jr. The method uses sampling tubes packed with 2,4-dinitro-phenylhydrazine (2,4-DNPH)-coated silica gel to absorb formaldehyde from the sampled gas. To draw the gas through the tubes, MRC used DuPont Model P200 portable sampling pumps set and calibrated to deliver a constant flow rate (±5%) of approximately 100 cc/min (actual pumps ranged from 92.3 - 107 cc/min) for long-term samples as suggested by Mr. David Haile, supervisor of the MRC industrial-hygiene certified laboratory. Short-term samples were collected using the same pumps set and calibrated at a constant flow rate (±5%) of approximately 200 cc/min (actual pumps ranged from 193.5 - 202.7 cc/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, formaldehyde sample blanks and spikes were used and all samples were analyzed and reported in accordance with standard MRC Quality Assurance/Quality Control procedures. Additional details on formaldehyde sampling and analysis methods are provided in Appendix C.

Sampling for methanol was conducted using a NIOSH-approved active dosimeter method, NIOSH 559. Silica gel tubes were used in conjunction with DuPont Model P200 and P30 pumps which were set and calibrated at a constant flow rate (±5%) of approximately 50 cc/min (actual pumps varied between 45.5 - 53 8 cc/min) for personal and source sampling and 30 cc/min (actual pumps varied between 25.8 - 37 cc/min), for area sampling, respectively. 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, five 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 methanol sampling and analysis procedures are included in Appendix C.

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 spiked blanks, 69 formaldehyde and 56 methanol samples were collected at Georgia-Pacific's Albany formaldehyde plant. The number and type of samples collected during the detailed survey are summarized in Table 2.

TABLE 2. FORMALDEHYDE AND METHANOL SAMPLES TAKEN DURING THE DETAILED INDUSTRIAL HYGIENE SURVEY OF THE GEORGIA-PACIFIC - ALBANY FORMALDEHYDE PLANT[a]

	Formaldehyde			Methanol	
	Long term	Short term	Spiked	Samples	Validation
Area	21	0	2	24	3
Personal	22	14	1	22	0
Source	7	1	1	5	2
Total	50	15	4	51	5

[a] Does not include blanks or spiked blanks taken once per shift - four spiked tubes for formaldehyde and the five validation tubes for methanol.

8.4 SAMPLING LOCATIONS

The locations where area, short-term personal, and source samples were taken are identified in Figures 36 and 37. Locations for long-term personal ampling are not shown because an operator during the sampling period would change location, making identification of long-term personal samples by location, inappropriate.

A description of sampling locations, including the number of samples taken at each location, is provided in Table 3.

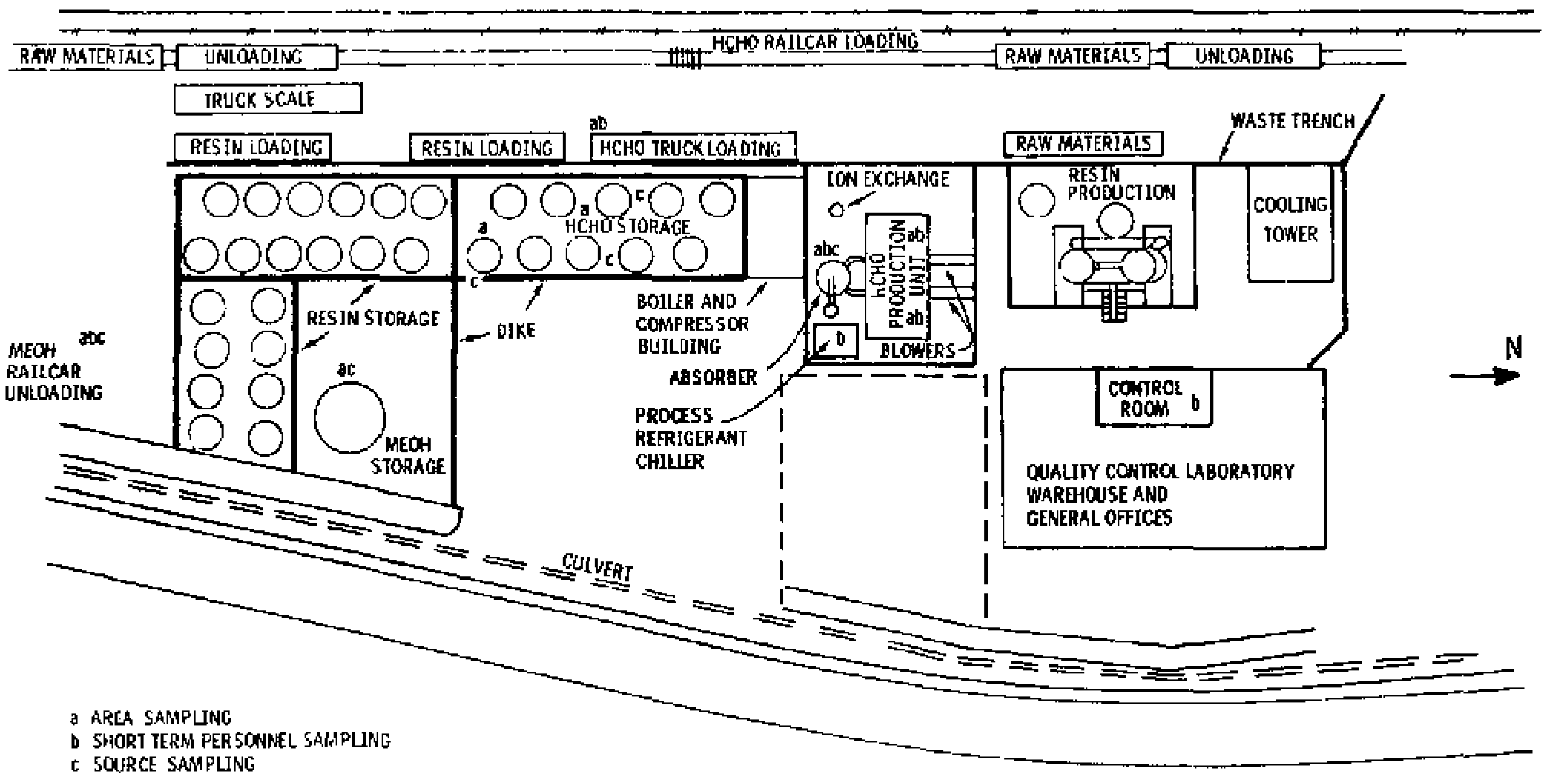

Figure 36 Locations of area, short-term personal, and source sampling conducted during the survey of Georgia-Pacific formaldehyde production plant in Albany, Oregon.

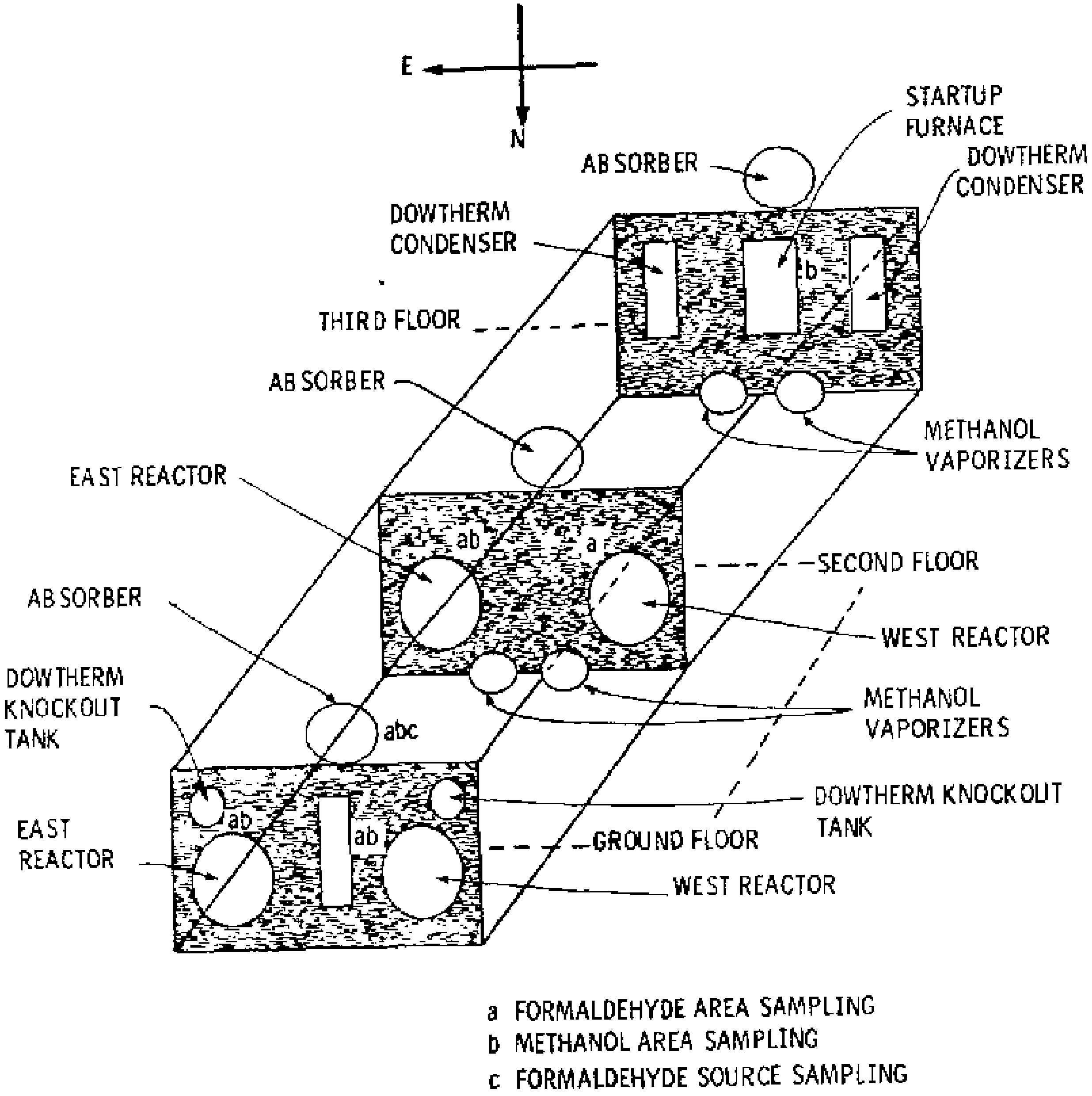

Figure 37. Locations of area and source sampling around the formaldehyde production unit.

TABLE 3. AREA AND SOURCE SAMPLE NUMBER AND LOCATION SUMMARY

Location	Number of samples	
	Formaldehyde	Methanol
Area		
East Dowtherm knockout tank	3	3
Center of ground floor near west converter	3	3[a]
North process sample point of absorber - ground floor	3	3
East converter electric outlet - 2nd floor	3	3
West converter electric outlet - 2nd floor	3[b]	0
Electric conduit beside propane furnace - 3rd floor	0	3
Methanol unloading area - S.W of pump	0	3
Formaldehyde storage area - E of tank F-3	2	2[c]
Formaldehyde storage area - E of tank F-5	2	2
Methanol storage area - between pump and inlet pipe	2	2
Source		
Formaldehyde storage tank F-8 - side agitator	1	0
Formaldehyde storage tank F-10 - side agitator	1	0
Formaldehyde absorber pump 2	3[b]	0
Formaldehyde loading pump	1	0
Formaldehyde absorber pump 1	1	0
Methanol storage pump 1	0	1
Methanol storage pump 2	0	2
Methanol unloading pump	0	2[a]

[a] Also, two methanol validation samples were taken at this location

[b] Also, a formaldehyde spike sample was taken at this location.

[c] Also, one methanol validation sample was taken at this location

SECTION 9

RESULTS

The tables that follow summarize the analytical results for samples taken by the MRC survey team at the Georgia-Pacific Albany, Oregon, plant during July 19-23, 1982. All volumes and concentrations have been corrected to standard temperature and pressure (68°F, 29 92 in. Hg). Tables 4 and 5 present long-term, personal sampling analytical results for formaldehyde and methanol. Short-term formaldehyde results are presented in Table 6. No short-term methanol samples were taken. Area sampling results are shown in Tables 7 and 8 and source samples are reported in Tables 9 and 10

In addition to analytical results, control room hood inward velocity measurements were taken with an Alnor Jr swinging vane anemometer and the average measured face velocities are summarized in Table 11.

TABLE 4 LONG-TERM FORMALDEHYDE PERSONAL SAMPLE ANALYTICAL RESULTS

Day	Shift	Description	Tube number	Flow[a] rate, cc/min	Sample time, min	Adjusted[b] volume (V), L	Concentration (C), ppm	TWA, ppm	Consecutive sampling period, min	Average[c] ppm
7/20	1	Operator 1	268	104	240	22.84	0.11			
7/20	1		425	104	181	17.22	0.70	0.36	421	
7/22	1		414	100.0	272	NA[d]	NA			
7/22	1		1,846	100.0	152	13.67	0.13	0.13	424	0.30
7/20	2	Operator 2	1,813	101.7	242	22.01	BDL[e]		-	
7/20	2		403	101.7	230	20.92	0.25	0.12	472	
7/21	2		60	100.8	252	22.89	0.28			
7/21	2		1,958	98.0	188	16.60	0.22	0.25	440	0.18
7/21	1	Operator 3	445	98.4	243	21.55	0.31			
7/21	1		1,294	98.4	176	15.61	0.13	0.23	419	0.23
7/22	2	Operator 4	1,762	101.7	243	22.22	0.02			
7/22	2		1,200	101.7	169	15.46	0.20	0.09	412	0.09
7/21	1	Maintenance worker 1	1,916	100.0	252	22.71	0.46			
7/21	1		1,131	100.0	200	18.02	0.11	0.31	452	
7/22	1		1,987	100.8	285	25.84	0.02			
7/22	1		70	100.8	138	12.51	0.24	0.09	423	0.20
7/21	1	Maintenance worker 2	1,960	101.7	246	22.55	0.59			
7/21	1		267	101.7	204	18.70	0.15	0.39	450	
7/22	1		1,939	103.4	280	26.03	2.22			
7/22	1		126	-	-	VOID	-	2.22[f]	280	1.10

[a] Pump flow rate was determined as follows within ±5% of calibration - assume initial flow rate, greater than ±5% but less than 15% - average initial and final flow rates, greater than 15% - dischard sample

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

[c] Average concentration - (Volume$_1$ Concentration$_1$ + V_2C_2 +)/(V_1 + V_2 +)

[d] Not analyzed

[e] Below detectable limit (0.01 ppm)

[f] Second sample voided due to method failure, result of one sample

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Note Operator and maintenance worker duties are described in Section 6

TABLE 5. LONG-TERM METHANOL PERSONAL SAMPLE ANALYTICAL RESULTS

Day	Shift	Description	Tube number	Flow[a] rate, cc/min	Sample time, min	Adjusted[b] volume (V), L	Concen tration (C), ppm	TWA, ppm	Consecutive sampling period, min	Personal[c] average ppm
7/20	1	Operator 1	1	49 8	122	5 56	12 09[d]			
7/20	1		4	49 8	304	13 86	BDL[e]	5 60	426	
7/22	1		43	51 7	273	12 69	BDL			
7/22	1		58	51 7	151	7 02	BDL	BDL	424	4 30
7/20	2	Operator 2	11	51 5	242	11 14	BDL			
7/20	2		20	51 5	171	7 88	BDL	BDL	413	
7/21	2		38	49 6	254	11 36	BDL			
7/21	2		42	49 6	186	8 32	BDL	BDL	440	BDL
7/21	1	Operator 3	23	50 0	241	10 86	BDL			
7/21	1		34	50 0	180	8 11	BDL	BDL	421	BDL
7/22	2	Operator 4	59	50 8	243	11 10	BDL			
7/22	2		60	50 8	169	7 72	6 73	4 53	412	3 76
7/21	1	Maintenance worker 1	21	52 2	253	11 91	BDL			
7/21	1		33	52 2	200	9 41	BDL	BDL	453	
7/22	1		44	51 1	285	13 10	BDL			
7/22	1		57	51 1	138	6 34	3 38	3 12	423	3 06
7/21	1	Maintenance worker 2	22	49 0	247	10 90	BDL			
7/21	1		32	49 0	205	9 05	BDL	BDL	452	
7/22	1		45	50 4	280	12 69	BDL			
7/22	1		56	50 4	134	6 07	BDL	2 31	414	BDL

[a] Pump flow rate was determined as follows <5% deviation - intial flow rate, 5% < x <15% - average initial and final flow rates, >15% - discard sample

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

[c] Average = $(\text{Volume}_1\ \text{Concentration}_1 + V_2C_2 + \quad)/(V_1 + V_2 + \quad)$

[d] Operator wore tube while unloading methanol tank car

[e] Below detectable limit (3 ppm)

TABLE 6   SHORT-TERM FORMALDEHYDE PERSONAL SAMPLE ANALYTICAL RESULTS

Description	Tube number	Flow[a] rate, cc/min	Sample time, min	Adjusted[b] volume (V), L	Concentration (C), ppm	Personal average, ppm	Activity[c] average, ppm
Formaldehyde process sampling and sample analysis							
Operator 1	1,990	200	16	2.88	0.15		
	1,112	200	16	2.93	0.12		
	291	200	22	4.03	0.08[d]		
	1,024	202.7	15	2.74	0.62		
	1,779	198.7	15	2.68	0.13		
	1,887	196.1	16	2.82	0.07	0.19	
Operator 2	1,279	200	16	2.86	BDL[e]		
	1,993	201.3	18	3.24	0.55		
	1,316	197.4	15	2.67	0.29		
	1,028	202.7	15	2.74	0.64	0.37	
Operator 3	74	196.1	19	3.35	0.29	0.29	0.26
Formaldehyde loading supervision							
Operator 2	1,842	193.5	39	6.79	1.04	1.04	
Operator 3	1,160	200	30	5.49	1.07		
	1,327	198.7	27	4.84	0.86	0.97	1.00
Gas sample at aftercooler							
Supervisor 1	1,853	198.7	35	4.48	1.34	1.34	1.34

[a] Flow rate was determined as follows <5% deviation - use in initial flow rate, 5% < x <15% - average initial and final flow rates, >15% - discard sample

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

[c] Activity average = $(V_1C_1 + V_2C_2 + \quad)/(V_1 + V_2 \quad)$

[d] Formic acid test - slightly different from other testing procedures

[e] Below detection limit

TABLE 7. FORMALDEHYDE AREA SAMPLING ANALYTICAL RESULTS

Description	Tube number	Flow[a] rate, cc/min	Sample time, min	Adjusted[b] volume (V), L	Concentration (C), ppm	Area[c] average, ppm
Breathing zone - adjacent to east dowtherm knock out tank - east edge of production area - ground floor ~4 ft east of reactor	287	98.4	241	20.37	0.20	
	1,340	98.4	241	22.72	0.13	
	1,328	100	249	21.00	0.31	0.21
Breathing zone - adjacent to center tank - center of ground floor - ~8 ft from east west converter - walkway to absorber	1,127	99.2	244	20.79	0.02	
	1,789	99.2	242	23.0	BDL[d]	
	1,287	97.6	249	20.49	0.05	0.03
Breathing zone - above north absorber sample point - ground floor	1,155	101.7	244	21.32	0.25	
	416	101.7	242	23.58	0.09	
	1,973	98.4	250	20.74	0.36	0.23
Breathing zone - west side of east converter electrical outlet - 2nd floor walkway to 2nd floor	1,783	100.0	237	20.36	0.64	
	1,207	97.6	247	20.33	0.10	0.37
Breathing zone - east side of west converter - electrical outlet - 2nd floor	1,700	100.0	238	20.45	0.20	
	30	100.0	238	22.80	0.11	
	1,924	99.2	245	20.49	0.08	0.13
Breathing zone - formaldehyde storage area - stand east of tank F3 - central location in storage area	424	98.4	254	21.11	0.78	
	1,307	98.4	235	22.32	0.56	0.67

(continued)

TABLE 7 (continued)

Description	Tube number	Flow[a] rate, cc/min	Sample time, min	Adjusted[b] volume (V), L	Concentration (C), ppm	Area[c] average, ppm
Breathing zone - formaldehyde storage area - east of F5 southern location in area - wind from NW	1,190	100 8	237	20.02	1 06	
	1,210	100 8	244	23.74	0.77	0 90
Breathing zone - methanol storage area - between pump #1 and inlet pipe southeast of formaldehyde storage-NW wind	1,844	100 8	227	19 33	0.32	
	294	100 8	248	24 14	0.55	0.45

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[a] Flow rate determined as follows. <5% deviation use initial flow rate; 5% < x <15% - average initial and final flow rates, >15% - discard sample

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

[c] Area average = $(V_1C_1 + V_2C_2 +. .)/(V_1 + V_2 + \ .\ )$

[d] Below detectable limit (0.01 ppm)

TABLE 8 METHANOL AREA SAMPLING ANALYTICAL RESULTS

Description	Tube number	Flow[a] rate cc/min	Sample time, min	Adjusted[b] volume (V), L	Concentration (C), ppm	Area[c] TWA, ppm
Breathing zone - adjacent to east dowtherm knockout tank - east edge of production area - ground floor ~4 ft east of east reactor	5	28	243	5 84	BDL[d]	
	14	28	238	6.38	BDL	
	48	32	249	6.72	BDL	BDL
Breathing zone - adjacent to center tank - center of ground floor - ~8 ft east of west converter - walkway to absorber	8	34 4	244	7.21	BDL	
	12	34 4	240	7.91	BDL	
	46	32 4	251	6 83	BDL	BDL
Breathing zone - above north absorber sample point - ground floor - west side of absorber	6	33	244	6 92	BDL	
	13	33	239	7.56	BDL	
	47	28 9	249	6 06	BDL	BDL
Breathing zone - west side of east converter - electrical outlet - 2nd floor - walkway to 2nd floor	9	34	240	7.01	>11 22[e]	
	15	34	237	7 72	>10.19[e]	
	49	32 8	248	6 85	BDL	15.12[f]
Breathing zone - electrical outlet on west side of propane furnace - 3rd floor	7	26 9	239	5 52	3 87	
	16	26 9	237	6 11	3 38	
	50	31 9	243	6 72	>11 37[e]	10.62[f]
Breathing zone - formaldehyde storage area - stand east of tank F3 central location in storage area	24	32 5	247	6 78	BDL	
	37	32 5	237	7 44	BDL	BDL

(continued)

TABLE 8 (continued)

Description	Tube number	Flow[a] rate cc/min	Sample time, min	Adjusted[b] volume (V), L	Concentration (C), ppm	Area[c] TWA, ppm
Breathing zone - formaldehyde storage area - east of tank F5 - southern location in storage area - wind from NW	25	28 4	236	5 66	BDL	
	35	28.4	244	6 69	BDL	BDL
Breathing zone - methanol storage area - between pump #1 and inlet pipe - southeast of formaldehyde storage - NW wind	26	29.3	225	5 51	BDL	
	36	29.3	249	7 05	BDL	BDL
Methanol unloading area - 3 ft from pump - 15 ft from tank cars - 3-1/2 ft above ground	3	50	176	7 56	BDL	
	31	32 4	117	3 42	BDL	
	54	47 8	144	6 19	BDL	BDL

[a] Flow rate determined as follows <5% deviation use initial flow rate, 5% < x <15% - average initial and final flow rates, >15% - discard sample

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

[c] $TWA = [(Volume_1)(Concentration_1) + V_2C_2 + V_3C_3]/[V_1 + V_2 + \quad]$

[d] Below detectable limit (3 ppm)

[e] Breakthrough occurred on the tubes - amount reported is minimum

[f] Assume double the measured values for samples in which breakthrough occurred

TABLE 9 FORMALDEHYDE SOURCE SAMPLING ANALYTICAL RESULTS

Description	Tube number	Flow[a] rate, cc/min	Sample time, min	Adjusted[b] volume (V), L	Concentration (C), ppm	Average concentration, ppm
Side agitator - Tank F8 tented w/plastic sheet and duct tape - apparent paraform, not in operation	38	100	238	22.8	>92.83[c,d]	>92.83[c,d]
Side agitator - Tank F10 tented w/plastic sheet and duct tape - no paraform, not in operation	1,719	98.4	236	22.25	>83.65[c,d]	>83.65[c,d]
Absorber pump #2 - in operation - tented w/ plastic and duct tape	433 1,794[e] 1,060[e]	102.6 97.2 98.4	124 119 117	10.75 11.17 11.11	14.78[c] >30.46[c,d] >33.15[c,d]	>26.33[c,d]
Loading pump - in operation tented w/ plastic and duct tape - used a dropout flask to prevent moisture buildup in tube	1,913[e]	101.0	33	3.22	>54.69[c,d]	>54.69[c,d]
Absorber pump #1 - in operation - tended w/ plastic and duct tape - used dropout flask to prevent moisture buildup in tube	1,090[e]	95.6	123	11.33	6.05	6.05

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[a] Flow rate determined as follows: <5% deviation - use initial flow rate, 5%< x <15% - average initial and final rates, >15% - discard sample

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

[c] Tube analysis indicated breakthrough - minimum value reported

[d] Slightly off calibration-extrapolated value

[e] Used a dropout flask to condense water and prevent moisture buildup in tube

TABLE 10 METHANOL SOURCE SAMPLING ANALYTICAL RESULTS

Description	Tube number	Flow[a] rate, cc/min	Sample time, min	Adjusted[b] volume (V), L	Concentration (C), ppm	Average[c] concentration, ppm
Methanol supply pump #1 - in operation - tented w/ plastic and duct tape	40	51.1	114	5.62	>273.67[d]	>273.67
Methanol supply pump #2 - in operation - tented w/plastic and duct tape	19	52.2	202	10.10	>62.56[d]	
	41	47.8	114	5.26	>125.94[d]	>84.3
Methanol unloading pump - in operation - tented w/plastic and duct tape - visible leak	28	51.1	124	6.12	>1,348[d]	
	52	51.1	146	6.29	>1,385[d]	>1,367

[a] Flowrate determined as follows <5% deviation - use initial flow rate, 5% < x <15% - average initial and final flow rates, >15% - discard sample.

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

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

[d] Breakthrough occurred - minimum value reported

TABLE 11. A SUMMARY OF CONTROL ROOM HOOD VELOCITY MEASUREMENTS

Hood window position	Average face velocity, fpm
Window fully open	114
Window pushed 1/2 of the way down	172

SECTION 10

CONCLUSIONS

10.1 FORMALDEHYDE EXPOSURE

10.1.1 Operator Long-Term Exposure

One personal sampler was worn by an operator for each of two consecutive 4-hour periods during each of the day and second shifts from Tuesday through Thursday. These samples were taken to evaluate an operators long-term exposure. A total of four operators were sampled. The total sample period for the sets of two consecutive samples worn by an operator ranged from 412 to 472 minutes It is felt that the results for these sample periods give a good indication of the operator exposure to formaldehyde during a work day. The results for each pair of samples have been averaged to yield an average exposure concentration for each operator sampled. The results are presented in Table 4, Section 9.

The concentration to which each operator was exposed to for an approximate seven-hour sampling period is less than 12% of the OSHA-time-weighted average permissible exposure limit (PEL) of 3 ppm Thus, the long-term operator exposure is considered to be nonexcessive and controlled for those days the exposure was evaluated.

10.1 2 Maintenance Personnel Long-Term Exposure

Two consecutive personal samples were taken on each of two maintenance personnel during each of two consecutive day shifts. The total sampling period for the sets of two consecutive samples ranged from 423 to 452 minutes. The sampler worn by a maintenance employee for the second consecutive sample on the second day was accidentally broken and the sample voided The sample concentrations of each pair of consecutive samples for a maintenance employee have been averaged. This average concentration gives a good estimate of each employee's full shift exposure. Sample results are presented in Table 4, Section 9.

Sample number 1939, the 280-minute sample taken on a worker on 7/22, had a measured concentration of 2.22 ppm, which is much greater than that of any other long-term personal sample taken This concentration is more than three and one-half times that for any other maintenance personal samples taken. The maintenance worker who wore this sample worked with the other maintenance worker sampled while constructing a roof over the refrigerator unit located at the southeast corner of the formaldehyde production unit It is expected that the concentration for sample number 1939 would be similar to the other maintenance personal sample concentrations, since no other work was done, such as leak repair. Since this sample concentration is much greater than that of the other maintenance personal samples taken, the sample result is not considered indicative for the period of time sampled

In addition, the sample concentration is not a good estimate of the time-weighted average exposure for an entire shift of 480 minutes, since the sample period was only 280 minutes. As a result, the analytical result of 2 22 ppm will not be included in evaluating a maintenance worker's shift exposure. (It should be noted that this result is still only 74 percent of the permissible OSHA level of 3 ppm)

The average full shift exposure concentrations for the two workers sampled range from 0.09 ppm to 0.39 ppm. These results are below (less than 15 percent of the OSHA TWA PEL of 3 ppm, and indicate nonexcessive exposures for those maintenance workers sampled. Although the workers were located at the refrigeration unit at the southeast corner of the production unit, they were not repairing formaldehyde leaks or working on the formaldehyde production process. If process-related maintenance activities were being performed (such as repairing pumps or seals), their exposure might have been excessive. If an excessive concentration were encountered, it would be considered a controlled exposure if proper respiratory protection, which is available, were worn.

10 1.3 Formaldehyde Loading

Three short-term personal samples were taken on operators during truck loading on Tuesday and Wednesday during the survey. The results are shown in Table 6, Section 9.

None of the sample concentrations exceed the OSHA ceiling limit of 5 ppm, with the highest exposure only 21% of this limit This indicates a nonexcessive exposure for the samples taken.

As stated previously, the operator was also loading resin cars during formaldehyde loading. The operator is only at the resin loading station a short period of time to start and stop loading. He spends the remainder of the time at the formaldehyde loading station. Thus, the exposure to residual formaldehyde release from the resin should be insignificant compared to that from formaldehyde solution loading. The formaldehyde concentration due to resin loading should insignificant compared to the exposure due to formaldehyde loading.

Condensed formaldehyde-water solution was seen escaping from the truck hatch during loading. This indicates an escape of formaldehyde gas. Since the wind was changing direction during the three samples taken, the operator did not stand continuously downwind of the formaldehyde gas escaping from the hatch. The industrial hygienist sampling team member did smell formaldehyde and experience burning eyes when standing in the contaminated air downwind from the hatch. If the operator were standing occasionally downwind of the hatch, exposure might exceed the ceiling limit of 5 ppm.

No rail cars were loaded during the survey. Thus, the formaldehyde exposure could not be quantitatively evaluated. It is expected that the operator's short-term exposure while at the car could potentially be greater than the exposure during truck loading This additional exposure may occur because the operator performs all loading tasks such as vent opening and sample withdrawal He would be closer to the formaldehyde source than when trucks are loaded

10.1 4 Formaldehyde Solution Sample Withdrawal and Analysis

10.1 4 1 Absorber Sample Analysis--

Nine short-term personal samples were taken on an operator during routine withdrawal and analysis of a sample from the absorber (numbers 1990, 1112, 1024, 1779, 1887, 1279, 1993, 1316, and 1028). The results of these samples can be seen in Table 6, Section 9.

The plant standard procedure was followed. The sample was drawn into an open test tube and was transferred to the control/lab room. A specific gravity test performed in the lab hood without the exhaust fan turned on. A 30-mL sample was poured from the test tube to an Erlenmeyer flask, and the flask was placed in an oven within the hood. The hood exhaust fan was then turned on, and the tube was rinsed out into the sink next to the hood.

The nine sample results ranged from a nondetectable concentration to 0.64 ppm These concentrations are all less than 15% of the OSHA ceiling limit of 5 ppm, indicating a controlled exposure when these samples were taken.

Sample number 1887 was taken utilizing all existing controls, including both engineering and work procedure controls. The test tube was immediately stopped after collecting the sample, the lab hood exhaust fan was immediately turned on after the test tube was placed in it, and the waste was dumped in the sink within the hood to control and residual formaldehyde gas in the waste being dumped. The formaldehyde concentration of sample number 1887 was only 0.07 ppm, which is lower than seven of the other eight concentrations measured. This indicates that implementation of all existing controls can reduce the exposure of the operator to a very low level.

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

One short-term personal sample was taken on an operator while analyzing a sample withdrawn from a loaded truck (sample number 291). The operator ran specific gravity, percent formic acid and percent formaldehyde tests on the sample. The specific gravity test was performed in the lab hood, while the percent formic and formaldehyde determinations were performed outside the hood. All formaldehyde waste was dumped down the sink outside the hood. The 22-minute sample resulted in a concentration of 0.08 ppm, which is less than 2% of the OSHA ceiling limit of 5 ppm. This sample shows a nonexcessive, short-term exposure.

Another short-term personal sample was taken on the lead operator who withdrew a sample from formaldehyde storage tank F2 into a jar, covered the jar, and returned to the control/lab room to titrate the sample to determine the percent formic and formaldehyde (sample number 74). The titrations were performed outside the lab hood. All formaldehyde waste was dumped into the sink next to the hood. The 19-minute sample resulted in a sample concentration of 0.29 ppm, which is 6% of the OSHA ceiling limit (5 ppm). This sample also shows a nonexcessive, short-term exposure.

10.1 5 Gas Sample Withdrawal and Analysis

One short-term personal sample was taken on the quality control supervisor while withdrawing a gas sample from the converter and injecting the sample into the gas chromatograph for analysis. The 25-minute sample gave the highest concentration results for any personal sample taken, 1.34 ppm. Possible reasons for this high exposure are· 1) the gas being sampled was under pressure, 2) it was also at a high temperature (approximately 250°C), which makes it more difficult to handle, and 3) it was sampled at nose height. Although the results are the highest, they are still below the ceiling limit of 5 ppm.

10 1 6 Formaldehyde Area Sampling

Two consecutive 4-hour area samples were taken in eight locations in the plant. A third 4-hour sample was taken on a second day at five of the locations. One sample was voided after it was found disconnected from the pump Sample times ranged from 227 to 254 minutes For two consecutive samples, the total time ranged from 475 to 489 minutes. Table 7 in Section 9 presents the analytical results of this sampling. These samples give a representative indication of area formaldehyde concentrations within the plant.

The production plant area samples (5 locations) range from below detectable limits (0 01 ppm) to 0.64 ppm. The highest concentration is 21.3% of the OSHA permissible exposure limit (PEL) of 3 ppm time-weighted average (TWA). Area time weighted averages range from 0.02 to 0.37 ppm, or less than 12.5% of the permissible exposure The results of this area sampling indicate that the engineering controls and natural ventilation of the production area were adequate to prevent excessive exposure to workers while in these areas during the period sampled.

Three locations were sampled in the plant storage area. Analytical results ranged from 0.32 to 1.06 ppm formaldehyde on individual analyses and from 0.45 to 0.90 ppm formaldehyde for an 8-hour TWA. This 8-hour TWA represents 15 to 30% of the OSHA PEL of 3 ppm TWA. Although these results are higher than those for the production area, the concentration levels are within the OSHA permissible exposure limits and indicate that the engineering controls in use and the natural ventilation of the area are sufficient to protect the workers from excessive exposure.

10.1.7 General Conclusions on Formaldehyde Exposure

The personal and area samples taken during the detailed industrial hygiene survey yielded exposure or potential exposure up to 30% of the OSHA PEL of 3 ppm TWA or 5 ppm ceiling, with 40 out of 53 samples below 17% (0.5 ppm and 0.85 ppm) of the respective permissible levels. None of the sampled areas showed excessive or potentially excessive concentrations during the survey, indicating that the applied work practices and control technologies were effective An exposure could be excessive for maintenance workers during leak or seal repair. Also, there is a potential for overexposure for the operator during truck or rail car loading.

10.2 METHANOL EXPOSURE

10.2 1 Operator Long-Term Exposure

Two consecutive personal samples were obtained for an operator during each of the day and second shifts from Tuesday through Thursday. The total sample period for each set of consecutive samples worn by an operator ranged from 412 to 440 minutes, an approximate seven-hour sampling period. It is felt that the average result for each two consecutive samples gives a good estimate of an operator's workplace exposure. These results are shown in Table 5, Section 9.

For the first sample result of 12.09 ppm listed for the day shift of 7/20, there was excessive breakthrough into the backup tube section. Thus, some of the methanol vapor passing into the tube may have passed out of the tube beyond the backup section without being collected. If there was 100% breakthrough, the minimum concentration reported of 12.09 ppm would be doubled to 24 18 ppm Even assuming 100% breakthrough for the first sample and a sample concentration of 24.18 ppm, the time weighted average concentration is still less than 9.07 ppm. This result is 4.5% of the OSHA TWA PEL of 200 ppm. Other average concentration results for the remaining operators ranged below the detectable limit of 3 ppm up to 4.53 ppm, which is less than 2.5% of the PEL. Sample results indicate a nonexcessive exposure for those samples taken.

10.2.2 Maintenance Personnel Long-Term Exposure

Two consecutive personal samples were obtained for each of two maintenance workers during the day shifts of 7/21 and 7/22 The total sample period for each set of consecutive samples worn by a worker ranged from 414 to 453 minutes, which approximates a seven-hour period. The average results for each set of two samples for a worker should give a good estimate of his exposure for the entire shift. The sample results for each worker are given in Table 5, Section 9.

All average concentrations are less than 2% of the OSHA TWA PEL of 200 ppm Since the workers were constructing a roof over the refrigeration unit at the southeast corner of the formaldehyde production unit, it is expected that the exposure was lower than if the workers had been repairing leaks. It is expected that even if leaks were being repaired, the exposure would be nonexcessive because the PEL is high, the duration of these repairs is usually short, and the workers take safety precautions in such cases.

10.2.3 Area Methanol Sampling

Two consecutive 4-hour area samples were taken in eight locations in the plant. A third sample was taken on a second day at five of the locations. Sample times ranged from 225 to 251 minutes for individual samples and from 474 to 484 minutes for the two consecutive samples. A ninth location had three nonconsecutive samples taken, ranging from 117 minutes to 176 minutes. This location, methanol unloading, is an intermittent operation and is only visited when unloading a tank car. Analytical results for the samples taken in these locations can be found in Table 8, Section 9.

The production plant area samples (5 locations) range from below detectable limits (3 ppm) to greater than 11.37 ppm. Breakthrough occurred on three of the methanol tubes used. If 100% breakthrough is assumed, the concentrations for these samples is doubled.

This yields a higher exposure potential, but is still less than 6% of the OSHA permissible exposure limit of 200 ppm. Nineteen of the 24 area samples were below detectable limits and an additional two were slightly over the limit (3.87 and 3.38 ppm), indicating that exposure potential in the production area is low. Concentrations in two areas of the production area were among the 5 analytical results above the detection limit. Both of these areas were on upper levels of the production area near the methanol vaporizer. These locations may indicate that the vaporizer is releasing methanol vapors, but this is not conclusive.

Three storage area locations showed no detectable methanol concentrations. Engineering controls and natural ventilation of the area appear to have prevented unacceptable concentrations of methanol in this area during the survey.

10.2.4 General Conclusions on Methanol Exposure

The personal and area samples taken during the detailed industrial hygiene survey yield very low exposures to methanol with only 9 of 44 samples measuring concentrations above detectable limits. The highest level measured including an assumed 100% breakthrough of the silica gel tube, would result in only 11% of the OSHA PEL (TWA 200 ppm). This shows that during the survey, the plant was well controlled through engineering and work practices and that it poses little excessive exposure threat to the workers under normal operating conditions

10 3 EVALUATION OF ENGINEERING CONTROLS

10 3.1 Formaldehyde Sampling

Table 9 in Section 9 presents the analytical results of the source formaldehyde sampling. Footnotes indicate that five of the seven samples taken had breakthrough into the backup section of the sample tubes. This breakthrough exceeded 100% for these five tubes, which indicates that the sampling volume was too large or the concentrations too high and that the values reported can only be used as rough "minimum" estimates of any values. In addition, these five concentrations exceeded the calibraton curve for the method, making extrapolation necessary for any numerical result. Thus, these concentrations are not indicative of the true concentrations for these sources except to indicate the high concentrations compared to personal and area samples.

The remaining test samples also indicate higher concentrations than any area or personal sample discussed earlier. This was anticipated, based on the enclosed volume from which the samples were taken and the close proximity of the potential leak points

Tube number 433 also exceeded the calibration curve for the analytical method, but it was within reasonable limits, so the reading is approximately correct.

Analytical results for mass released per day are summarized in Table 12. These results assume that the concentration released was constant within the volume and that the leak rate from the controls was constant.

TABLE 12. MASS LOADINGS RELEASED FROM SOURCES

Source description	Tube no.	HCHO mass, µg	Sampling time, min	Daily release rate, g/d
Absorber pump #1	1,090	84.02	123	9 8 x 10^{-4}
Absorber pump #2	433	194.86	124	2.26.x 10^{-3}
	1,794[a]	417.48	119	5.05 x 10^{-3}
	1,060[a]	451.85	117	5.56 x 10^{-3}
Loading pump	1,913[a]	216.06	33	9.43 x 10^{-3}
Side agitator tank F-8	38[a]	2,596.9	238	15.7 x 10^{-2}
Side agitator tank F-10	1,719[a]	2,283.7	236	13.9 x 10^{-2}

[a] Breakthrough occurred - values reported are minimum.

These samples indicate a low release rate for formaldehyde from the absorber pumps. Unfortunately, this cannot be assumed for the other out-of-calibration/breakthrough results. If 100% breakthrough is used as a minimum number, the release rate for absorber pump #2 ranges from 2.26 x 10^{-3} g/d to 11.1 x 10^{-3} g/d and up to 18.9 x 10^{-3} g/d for a similar pump used for loading formaldehyde onto trucks. Thus, release rates for these pumps must be considered higher than these values indicate, by an undetermined amount.

No time evaluation of these controls (pump and agitator seals) can be made as a result of the large concentrations reported in the samples that overwhelmed standard sampling tubes and analytical methods. Based on the samples taken, it can be concluded that the pumps and agitators sampled are a source of formaldehyde emissions. From the area samples discussed earlier, it can be concluded that potential emission points are sufficiently controlled to maintain formaldehyde exposure to permissible levels However, no conclusion can be made on the effectiveness of leak prevention at individual points.

10.3.2 Methanol Sampling

Table 10 in Section 9 presents the analytical results of the source methanol samples Footnotes indicate that breakthrough occurred on all five sampling tubes. Breakthrough ranged from 38 8% to 53%. Concentrations on the tubes did not exceed the capacity of the methanol tubes (∿900 mg/m^3 = 687 ppm) Methanol breakthrough in the tubes was not anticipated and is not clearly understood at this time. It has been proposed that methanol migration occurred due to humid conditions during storage This possibility is currently being investigated under controlled situations.

The methanol breakthrough in the tubes creates a problem similar to that discussed for the formaldehyde samples. However, in this case, the concentrations are within the calibration limits and breakthrough on the back sections of the tubes is less than 100%. If we assume that the breakthrough is real, a portion of the methanol may have been released from the tubes. Thus, the concentrations reported are minimum values. Table 13 presents the minimum release rate for methanol from the controls tested.

The table values indicate a low daily release rate ranging from 5.8×10^{-3} g/d to 1.255×10^{-1} g/d. These release rates are not high enough to create a large envelope of concentration around the controls which exceeds the permissible concentration of 200 ppm. Methanol exposure was adequately controlled by the engineering controls (i.e., pump seals) during the survey.

TABLE 13. MINIMUM METHANOL RELEASE RATES FROM ENGINEERING CONTROLS

Description	Tube no.	MeOH mass, µg	Sampling time, min	Break-through, %	Daily release rate, g/d
MeOH supply pump #1	40	2,013	114	38.8	2 55 x 10^{-2}
MeOH supply pump #2	19	827	202	48.0	5.8 x 10^{-3}
	41	867	114	44.4	1.1 x 10^{-2}
MeOH unloading pump	28	10,800	124	53.0	1.255 x 10^{-1}
	52	11,400	146	52.0	1.125 x 10^{-1}

10.4 FINAL CONCLUSIONS

The Georgia-Pacific Albany, Oregon formaldehyde production plant uses work practices, engineering controls, and natural ventilation to control worker exposure to formaldehyde and methanol to acceptable levels. In most cases, formaldehyde exposure is below 20% of the OSHA permissible exposure limit of 3 ppm 8-hr TWA and the OSHA short-term exposure limit of 5 ppm. The nine areas sampled were within these limits. Engineering controls appear to maintain low levels of formaldehyde in the work environment, but no exact conclusions can be made regarding the amount of emissions. It appeared that the natural ventilation of the area including a fairly constant wind during the survey, affected the concentration more than the engineering controls. It is expected that the engineering controls would be adequate to maintain formaldehyde concentrations below acceptable limits when no wind is present.

SECTION 11

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APPENDIX A

VESSEL AND TANK ENTRY PROCEDURE

NEVER enter any tanks, vessels, tank trucks, or piece of equipment without:

(1) Informing immediate supervisor of intention to enter the equipment.

(2) Making positive that all electricity to moving mechanical parts is shut off by using the proper Electrical Lockout procedure or Tag/Lockout procedure.

(3) Wearing the proper safety clothing <u>with safety belt and rope attached</u>.

Don't be a

Chance Taker

(4) Having a helper standing outside the tank, vessel, or piece of equipment dressed in like fashion ready to assist if needed.

(5) Having the helper positioned in a place where he can watch and immediately assist if needed.

(6) Having self-breathing equipment on the immediate site for instantaneous use.

(7) Having thoroughly planned the operation or task and communicating this plan to the helper before entering the vessel.

(8) Check tank with explosimeter for oxygen content and/or explosive ranges.

(9) Shut and tag out all valves which could unexpectedly fail and spill on personnel inside vessels or tanks.

VIOLATION OF THE PRECEDING RULES WILL RESULT IN AN AUTOMATIC 1 - 2 DAY SUSPENSION WITHOUT PAY

APPENDIX B

PROCEDURE FOR ENTERING TANKS, VESSELS, OR CONFINED AREAS

No person shall enter a manhole, tank, or vessel without the approval of his supervisor or the department supervisor.

Prior to such entry:

1. Management shall designate an individual who shall be responsible for the safety of the employees and institute such means, methods, and practices as to render the work, and place of work safe. The designated person shall ascertain that the written procedures are followed.
2. Each vessel, tank, or confined area shall be purged and/or ventilated as thoroughly as practical.
3. Liquid and steam valves shall be closed and locked. Lines will be blanked and locked when the line contents and/or volume present a hazard.
4. All electrical circuits to agitators, pumps, etc , shall be locked out.
5. The atmosphere within the vessel, tank, or confined area will be tested for explosive vapors, suspected toxic agents, and adequate oxygen.
6. Electrical circuits leading into the vessel, tank, or confined area where conductive hazards exist shall be protected by a "ground fault interrupter" or the voltage shall not exceed 24 volts.
7. All safety equipment necessary shall be at the job site and shall be inspected and/or tested to assure that it functions properly.
8. An attendant shall remain outside at the opening of the confined area to render assistance necessary to the persons inside.
9. Tests shall be conducted at reasonable intervals, as work progresses, by a person thoroughly trained and instructed in the use of the instruments required. Types of solvents and/or cleaners in use shall be considered when determining "reasonable intervals."

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Plant Manager
Albany Chemicals-Resins
Georgia-Pacific

APPENDIX C

FORMALDEHYDE AND METHANOL SAMPLING AND ANALYSIS METHODS

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

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

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

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

EXPERIMENTAL

Reagents. Formaldehyde (37%), dimethyl formamide, and hydrochloric acid were Fisher Certified ACS grades. Acetonitrile was Burdick & Jackson distilled in glass. Silica gel was from Aldrich (Catalog No. 21 441-5, Grade 15, 35-60 mesh).

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

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

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

The HPLC system used was a Waters Model 6000A pump, a Rheodyne Model 70-10 injection valve with Model 70-11 loop filler port and 50-μL fixed volume loop, a Waters Model 440 UV visible absorbance detector fitted with a 340 nm wavelength kit, and a Houston Instrument Omniscribe B 5000 recorder fitted with a Spectrum 1021A filter and amplifier. A Waters C_{18}/Corasil guard column was used with a Supelco Supelcosil LC-8 (150 × 4.6 mm) analytical column.

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

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

Generation of Formaldehyde Standard. Permeation tubes of α-POM were prepared using 40 mg α-POM per cm of active tube length in 1/4-in. o.d. Teflon tubing (1 mm wall thickness). Both the α-POM tubes and the purchased paraformaldehyde tubes were used successfully to generate a dynamic standard of formaldehyde in air, as judged by excellent correspondence of weight losses with responses obtained by the present sampling and analytical procedure. The permeation chamber was held at 98 °C for α-POM and at 79 °C for paraformaldehyde. Permeation rates were 443 ng/min/cm and 96 ng/min/cm, respectively.

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

Silica gel, 12.5 g, is placed in a 100-mL round bottom (RB) flask, followed by 12.5 mL of 6 N HCl. DMF, 40 mL, is added to a 50-mL volumetric flask containing 5.0 g 2,4-DNPH. This mixture is swirled 10-15 s, quickly diluted to the mark with additional DMF, and immediately poured through a glass wool plug in a funnel into the flask containing the silica gel and HCl. The volumetric flask and glass wool are rinsed with an additional 5 mL of DMF, which is also added to the RB flask. The mixture is allowed to stand for 30 min, with occasional swirling, before isolation by vacuum filtration. The coated silica gel may be rinsed sparingly with DMF (2-3 mL). Excessive washing will result in decreased capacity for formaldehyde. It is left on the filter paper with continued suction for 1-2 min and then transferred quickly to a 100 mL RB flask. It is dried under vacuum at 5[illegible] °C for 1 h, with brief turning every 10 min. Continuous turning, as on a rotary evaporator, was found to grind the particles too finely and result in unacceptable back pressure in subsequent air sampling. Much longer drying times, as overnight, apparently completely remove residual DMF and result in decreased collection efficiency.

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

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

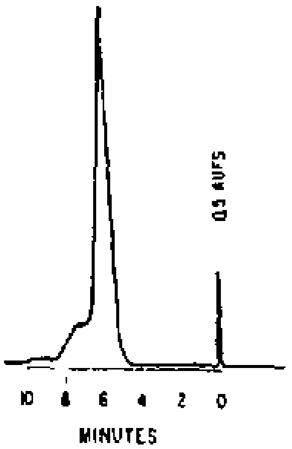

Figure 1. HPLC chromatogram for injection of 4.6 μg of formaldehyde-2,4-dinitrophenylhydrazone (equivalent to 1.08 ppm formaldehyde in air for a 20-L air sample).

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

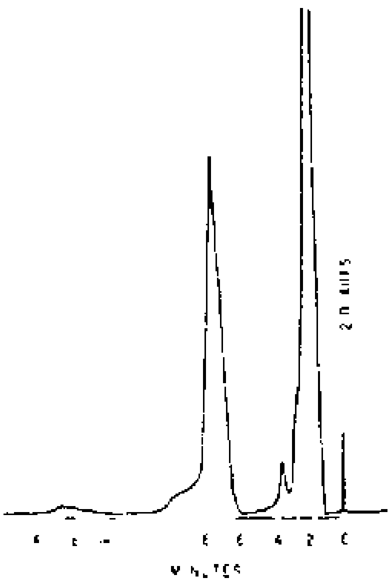

Figure 2. HPLC chromatogram for injection of sample resulting from collection of 122 μg of formaldehyde (4.96 ppm for a 20 L sample) on a 2,4-DNPH coated silica gel tube as described in the Experimental section.

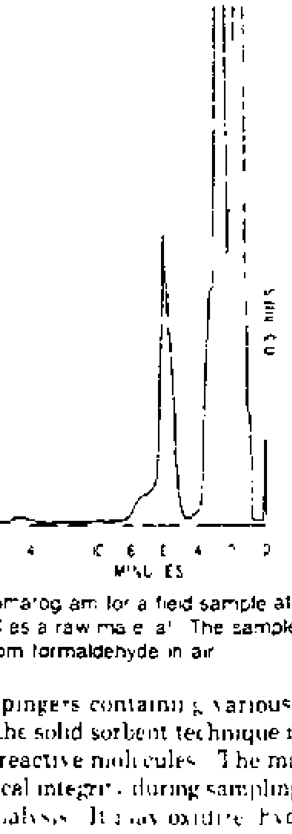

Figure 3. HPLC chromatogram for a field sample at a location where formaldehyde is used as a raw material. The sample was determined to represent 0.85 ppm formaldehyde in air.

posed by glass impingers containing various liquids.

Unfortunately, the solid sorbent technique is often difficult to do with highly reactive molecules. The material may not maintain its chemical integrity during sampling or subsequent storage prior to analysis. It may oxidize, hydrolyze, polymerize, or undergo other transformations. Wood and Anderson (7–9) 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 10 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, 330, 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
2.01	1.89	93	0.049
3.78	3.61	96	0.040

[a] Based on a 20-L air sample. Amount based on weight loss of permeation tube and time of collection at constant rate. [b] Average of six samples. Measurements were tested for outliers by Grubbs' test (*19, 20*) at the 99% confidence level. [c] Pooling of the individual RSDs gives the result of 0.037 with a χ^2 value from Bartlett's test (*19, 21*) of 49.50. Omitting the RSD at the 0.09 ppm level results in a pooled RSD of 0.041, with χ^2 of 0.62 (critical values for χ^2 at the 0.01 level are 13.28 for four degrees of freedom and 11.34 for three degrees of freedom).

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

A small background peak, equivalent to ~0.08 ppm CH_2O for a 20-L air sample, was routinely present in blank samples prepared in the laboratory. One source of contamination that was observed and should be avoided is Bakelite bottle caps. Bakelite, of course, is a polymer prepared from formaldehyde and phenol. Apparently enough free formaldehyde is available to cause a low level background.

Validation. The method was laboratory validated by generating six samples at each of five levels equivalent to 0.1–3.8 ppm formaldehyde for a 20-L air sample. The results are summarized in Table I. Average recovery was 94%. The pooled coefficient of variation, or relative standard deviation, was 0.04. Precision at the lowest level is probably artificially good due to the inadequacy of the peak height measurement at this level. A linear regression of formaldehyde expected vs. found showed excellent correlation, with a slope of 0.95 and an intercept of -0.01 ppm.

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

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

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

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

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

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

Field Tests. The performance of this method was evaluated in several tests at three industrial locations where formaldehyde is used as a raw material in two widely different processes and where a great diversity of other chemical processes are in operation nearby. Approximately 75 samples were taken. No sampling or analytical problems were observed. No breakthrough into a back-up section was found. The largest loading was 108 µg formaldehyde, obtained over a period of 3.0 h at 113 mL/min (ambient temperature, ~32 °C; relative humidity, 51%).

Some additional field results are discussed in the next section.

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

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

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

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

The results from one field study are shown in Table II. Four solid sorbent tubes and four impinger assemblies were set at the same sampling location. The various devices were within a few inches of each other but the sampling inlets were not in intimate contact. The mean of the solid sorbent results was 2.2 ppm, with a standard deviation of 0.3 ppm. The mean of the impinger results was 1.6 ppm, with a standard deviation of 0.2 ppm. An unpaired T test showed that these results were statistically different at the 95% confidence level.

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

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

replicate no	formaldehyde found, ppm	
	from coated gel	from impinger
1	2.4	1.7
2	1.9	1.9
3	1.9	1.4
4	2.4	1.4
	$\overline{X}$ = 2.2, σ = 0.3	$\overline{X}$ = 1.6, σ = 0.2

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

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

sample type	no of samples	CH_2O spiked, ppm	total CH_2O found, ppm	ambient CH_2O concn (total minus spiked) ppm
coated silica gel	3	0.86	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).

ACKNOWLEDGMENT

We are grateful to P. M. Jeannot and D. F. Tomkins for supplying us with the information on the relative position of the hydrazone shoulder on different HPLC columns.

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Formaldehyde Sampling Procedures:

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

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

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

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

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

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

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

Methyl Alcohol

Analyte	Methyl Alcohol	Method No. S59
Matrix	Air	Range. 140-540 mg/cu m
OSHA Standard	200 ppm (260 mg/cu m)	Precision ($\overline{CV}_T$) 0.070
Procedure	Adsorption on silica gel, desorption with water, GC	Validation Date 1/17/75

1. Principle of the Method

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

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

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

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

2. Range and Sensitivity

2.1 This method was validated over the range of 140-540 mg/cu m at an atmospheric temperature and pressure of 25 C and 745 mm Hg, using a nominal 5-liter sample. Under the conditions of sample size (5 liters) the probable range of this method is 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 8.9% lower than the "true" value at the OSHA standard level.

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

5 Advantages and Disadvantages of the Method

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

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

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

6. Apparatus

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

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

6.3 Gas chromatograph equipped with a flame ionization detector.

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

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

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

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

6.8 Pipets: 1.0-ml delivery type.

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

7. Reagents

7.1 Eluent: Distilled water

7.2 Methyl Alcohol (reagent grade).

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

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

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

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

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

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

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

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

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

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

8.4 Analysis of Samples

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

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

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

1. 30 ml/min (60 psig) nitrogen carrier gas flow
2. 30 ml/min (50 psig) hydrogen gas flow to detector
3. 300 ml/min (50 psig) air flow to detector
4. 200 C injector temperature
5. 300 C manifold temperature (detector)
6. 80 C column temperature

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

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

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

8 5 Determination of Desorption Efficiency

8 5.1 Importance of determination The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of silica gel to another Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process.

8.5.2 Procedure for determining desorption efficiency. Silica gel equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2 0-ml sample container. This silica gel must be the same type as that used in obtaining the samples and can be obtained from unused silica gel tubes. A known amount of the analyte is injected directly into the silica gel with a 10-μl syringe, and the container is capped. The amount injected is equivalent to that present in a 5-liter sample at the selected level.

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

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

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

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

9. Calibration and Standards

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

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

10. Calculations

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

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

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

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

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

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

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

10.6 Another method of expressing concentration is ppm

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

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)