

MRC-DA-1148

DETAILED INDUSTRIAL HYGIENE SURVEY  
FORMALDEHYDE PRODUCTION

114. 196

Celanese Chemical Company, Inc.  
P.O. Box 428  
Bishop, Texas 78343

Participants

David W. Dunn, Mark L. Johnson, Leroy Holmes  
and William H. Hedley  
Monsanto Research Corporation  
Glen J. Barrett, CIH, GEOMET Technologies, Inc  
William N. McKinney, Jr., C.I.H., NIOSH

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MONSANTO RESEARCH CORPORATION  
DAYTON LABORATORY  
Dayton, Ohio 45407

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## GLOSSARY OF TERMS

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

## GLOSSARY OF TERMS (continued)

double mechanical seal	a multiple seal arrangement that uses two single mechanical seals oriented back-to-back with a fluid filled space between them
engineering controls	the physical modification of a process or equipment used to reduce or prevent the release of contaminants into the plant area
EPA	Environmental Protection Agency
exposure	respiratory, eye, or skin contact with a contaminant
face velocity	the time rate of change of position of air at the front open face of a hood
formalin	formaldehyde solution
fpm	feet per minute
GC	gas chromatograph
gpm	gallons per minute
GTI	GEOMET Technologies, Inc., Rockville, MD
HCHO	chemical formula for formaldehyde
IH	industrial hygiene
L	liter
long-term exposure	contact with a concentration of contaminant during a long-term task
long-term sample	collection of contaminant occurring during a long-term task
long-term task	an operation or worker activity that requires an extended period of time to complete, usually a full work shift
MeOH	symbol used for methanol
min	minute

GLOSSARY OF TERMS (continued)

mL	milliliter
MO	methanol oxidation
MRC	Monsanto Research Corporation, Dayton, OH
NA	not analyzed due to uncontrolled circumstances
ND	not detected; no indication of compound found during analysis
NIOSH	National Institute for Occupational Safety and Health
nonexcessive exposure	contact with contaminant that does not exceed the OSHA regulation
OSHA	Occupational Safety and Health Act
OSHA HCHO STEL	the concentration of HCHO which should not be exceeded even instantaneously, which is 5 ppm
OSHA HCHO TWA PEL	the time-weighted average concentration of formaldehyde which should not be exceeded in an 8-hour work shift of a 40-hour work week - limit is 3 ppm
OSHA MeOH TWA PEL	the time-weighted average amount of methanol which should not be exceeded in an 8-hour work shift of a 40-hour work week - limit is 200 ppm
packed seal	an engineering control used to control emissions from nonstationary equipment parts. Normally consists of material within a packing gland that seals potential leaks when compressed
PEL	permissible exposure limit; the time-weighted average concentration to which nearly all workers may be repeatedly exposed, day after day, without adverse effect
personal sample	the collection of a volume of potentially contaminated air from the breathing zone area of a worker

## GLOSSARY OF TERMS (continued)

PIHS	preliminary industrial hygiene survey, an in-plant survey conducted in order to gain approximate information on worker exposure, work practices, engineering controls, process flow, and the plant safety and health program
ppe	personal protective equipment; equipment worn by a worker, as a respirator, used to prevent potential worker over-exposure to a contaminant
ppm	parts per million
short-term exposure	contact with a concentration of contaminant during a short-term task
short-term sample	collection of contaminant during a short-term task
short-term task	an operation or specific worker activity, the duration of which is part of a full work shift. The duration of the task normally ranges from 10 minutes to 2 hours.
single mechanical seal	the use of two sealing surfaces perpendicular to a shaft, one stationary, one rotating, to prevent leaks
source sample	an air sample taken at a fixed location within an artificially isolated area of an engineering control device. Used to estimate the expected release rate from that device.
standard conditions	temperature and pressure conditions to which the volume of all samples is adjusted so as to allow sample concentration comparison. Conditions used were 20°C (68°F) and 760 mmHg (29.92 in. Hg)
STEL	short term exposure limit; a short term concentration limit set for contaminant exposure

GLOSSARY OF TERMS (continued)

TWA                    time-weighted average, the average concentration of a sample or a set of consecutive samples, weighted by the time sampled

walk through survey    a preliminary industrial hygiene survey

## 1. INTRODUCTION

The following detailed industrial hygiene survey report describes a five-day survey conducted at the Celanese Chemical Company, Inc., formaldehyde production plant located near Bishop, Texas. This plant uses a metallic silver catalyst to convert methanol to formaldehyde at a rated capacity of approximately 1,500 million pounds of formaldehyde per year. The plant was selected for detailed study based on its good and unique 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) P.E., CIH, and David Dunn, Mark Johnson, and Leroy Holmes (Monsanto Research Corporation) on October 11-15, 1982. Personnel contacted during the visit were William Meyer, Safety, Health, and Environmental Manager; Mark Stenzel, Corporate Industrial Hygienist, Gary Ille, plant Industrial Hygienist; Chuck Gary, Chemist; and Joann Glenister, Chemist. Other plant management personnel were involved in short meetings discussing this project but were not significantly involved in the survey. Eleven workers were sampled for formaldehyde and/or methanol during the survey. The Celanese personnel listed above observed and conducted side-by-side sampling during the survey.

## 1.2 SUMMARY OF ACTIVITY

The survey team met with plant management personnel on Monday, October 11, to discuss the purpose of the survey, desired results, activities to achieve these results, and the report that would result from this survey. Arrangements for cooperation with the survey team were made at the meeting. A second short meeting with the technical personnel was held to organize the activities and the side-by-side sampling.

The survey team set up a base of operations in the main laboratory for the plant. Sampling was started by mid-day on Monday, and continued through 3:00 p.m., on Friday, October 15 (four day shifts, four second shifts). No sampling was conducted during the third shift due to logistics and similarity of process operation on all shifts.

Personal exposure samples for formaldehyde and/or methanol were taken by sampling four operators, two loader operators, one blending operator, and four maintenance personnel. 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 the control equipment.

Unfortunately, the quality assurance checks on the formaldehyde samples indicated that these results were unreliable. Hence, all of the formaldehyde results were discarded.

Table 1 shows the total number and types of sampling conducted for methanol during the five-day survey.

TABLE 1. METHANOL SAMPLES COLLECTED DURING IH SURVEY AT CELANESE CHEMICAL COMPANY, INC., BISHOP, TX, OCTOBER 11-15, 1982.<sup>a</sup>

Type	Number of methanol samples
Personal	9
Area	19
Source	<u>7</u>
Total	35

<sup>a</sup>Does not include blanks and spikes taken for QA/QC.

Observations of operator procedures and activities were also made during the survey. Control and process equipment were noted and discussed with the engineering and maintenance personnel. Pictures were taken of many operator activities and equipment used.

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

## 2. BACKGROUND

### 2.1 GENERAL

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

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

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

The objectives of the IH/CTA study are to:

- a. evaluate the state-of-the-art control technology in the formaldehyde production industry,
- b. evaluate the effectiveness of industrial hygiene control programs to control these potential hazards,

- c. identify potential hazards to workers,
- d. evaluate these potential hazards for the effects on workers,
- e. assess current formaldehyde production technology with respect to control of potential exposures of workers,
- f. assist the transfer of control technology inter- and intra-industry, and
- g. identify processes for which engineering controls are not available or are ineffective, where further research and development are needed, and to indicate priorities for application of control technology.

The study 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.

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

- observation of operator work practices,
- quantitative personal sampling.

- evaluation of engineering control techniques, monitoring devices, and personal protective equipment used by the industry to reduce exposures, and
- preparation of a detailed plant visit report for each of the four surveys, detailing worker practices and evaluating the engineering controls used by the plant; this report is one of these four reports.

### 3 DESCRIPTION OF THE PLANT

The Celanese Chemical plant is located in a rural area of Texas, approximately two miles from Bishop. The plant, originally built in 1945, is located on a site of approximately 1,300 acres and produces an assortment of chemicals and plastics. The formaldehyde production facilities, which are part of the chemical plant, operate continuously and have a total annual capacity (1980) of  $1,500 \times 10^6$  lb/yr of 37 percent formaldehyde solution. Formaldehyde is used captively or sold as formalin and shipped by truck or rail.

Four methanol oxidation (MO) units are used to produce formaldehyde. These units are not enclosed due to the mild climate throughout the year. Open air construction provides for good natural ventilation and control of air contaminants through dilution. Each methanol oxidation unit has a separate, enclosed control room equipped with a small laboratory for process sample analysis. The first formaldehyde production unit was built in 1962, two more in 1969, and the fourth has recently been brought on line.

The plant work force is nonunionized and operates by using four shifts. The formaldehyde production work force consists of four shift supervisors with four operators per shift (one per MO unit per shift); one extra operator fills in where needed over all four shifts. Personnel involved with the MO units total 21. In addition, there are nine loader operators to load tank trucks and cars for the entire plant. These employees load all products, including formalin. The plant also employs 120 maintenance workers that work during the day shift throughout the plant.

The production operators are responsible for operating a single MO unit and monitoring the unit for possible problems. Their duties includes minor maintenance, process sampling and analysis, and spill control and cleanup. Operators are also responsible for reporting major mechanical problems to maintenance.

Figure 1 is a rough schematic of the plant area surveyed. The survey was limited to a single MO unit (MO-2) and the plant storage and loading areas.

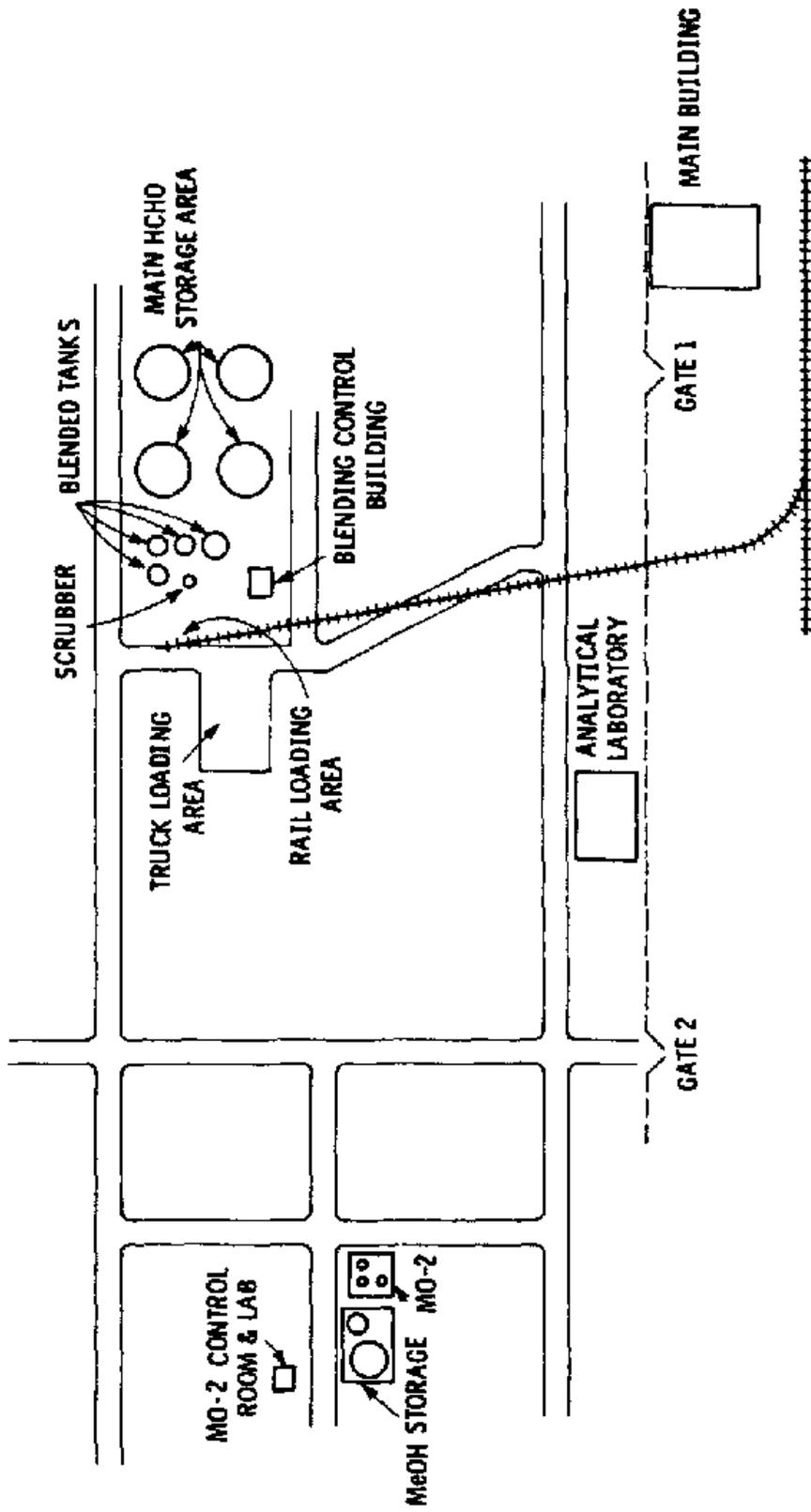


Figure 1. Approximate diagram of the Celanese plant area involved in the IH survey.

#### 4. PROCESS DESCRIPTION

Figure 2 presents a typical process schematic of a formaldehyde production unit. Methanol is received from a methanol synthesis unit and held in storage tanks. The methanol is transferred from a storage tank, through a filter and a preheater (heat recovery unit), and then to a vaporizer. Air is simultaneously drawn through an air filter by a blower. The filtered air and vaporized methanol are combined and transported through a closed system to the reactor. Formaldehyde is produced within each reactor using a silver catalyst. The product gas passes through a heat recovery unit by which the methanol is vaporized. The product gas is passed to an atmospheric absorber column in which water is passed from the top to bottom through the absorber, with the product gas entering the bottom and passing upwards. The liquor is cooled by recirculation through heat exchangers. Unabsorbed gas is vented off the top of the absorber, through a flame arrestor to an incinerator, which is used to generate steam.

The liquor from the absorber is transported to an atmospheric distillation column. Air vented off the top of the distillation column, which consists of water vapor and a trace of formaldehyde and methanol, is directed to the vaporizer. Formaldehyde solution from the still, which is approximately 50 percent by weight, is then directed through a heat exchanger and a cartridge filter, to formaldehyde storage tanks. In order to reduce formation of paraformaldehyde in storage tanks, the product is circulated through a heat exchanger to maintain a product temperature of about 60°C. The MO-2 unit has two parallel processes including vaporizers, air filters, reactors, and heat exchangers that feed a common absorber.

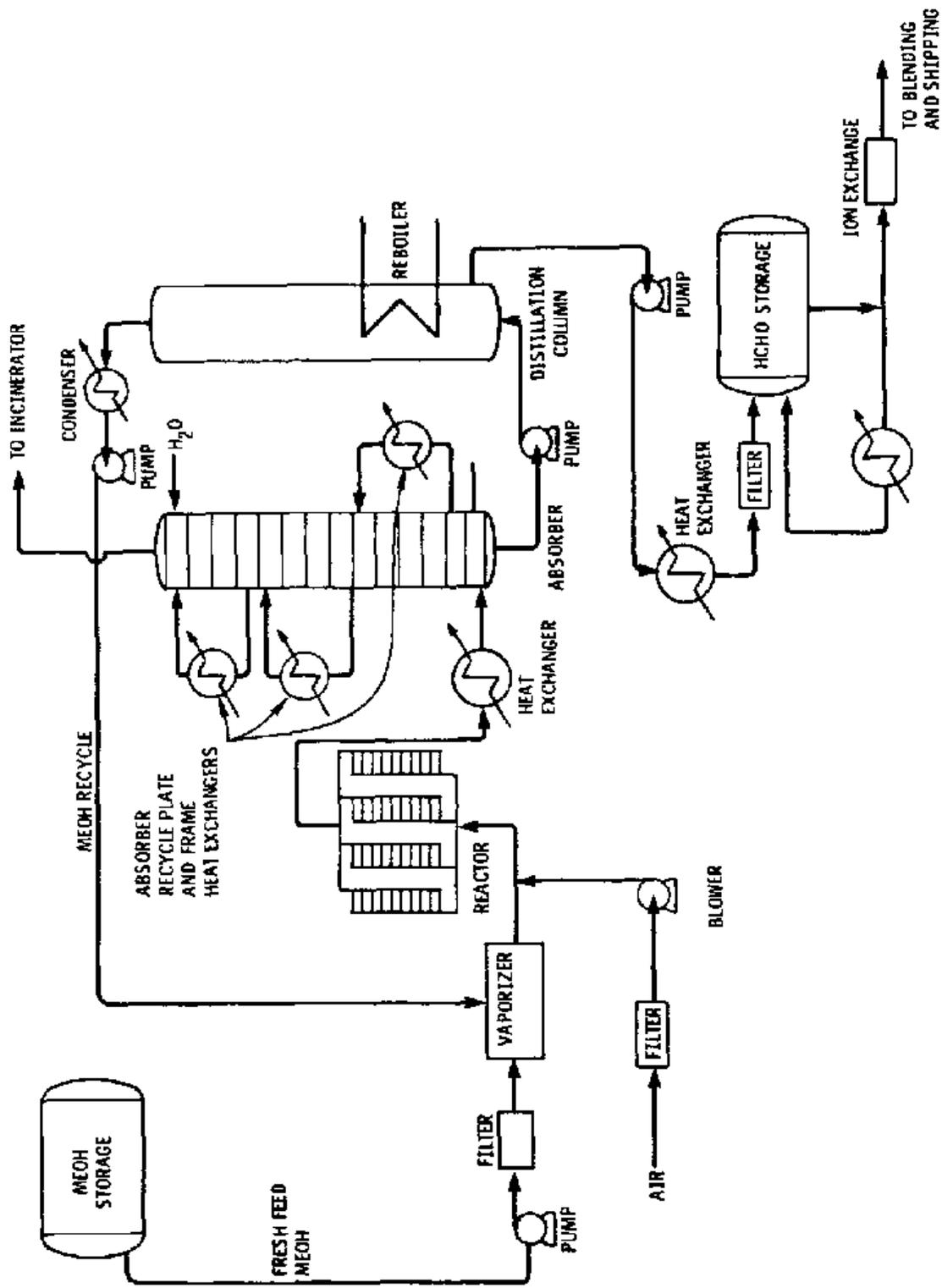


Figure 2. Typical silver process schematic

Formaldehyde samples are drawn from the system by the operator at the absorber, the distillation column, and at the recycling line between formaldehyde storage and the production circulation heat exchanger. Samples are normally collected twice per shift. The samples are collected by manually opening ball valves at these points and filling an Erlenmeyer flask. The flask is then hand-carried to a production lab for analysis

Blending is done with automatic controls from an isolated control room, with loader operators manually placing feed lines on rail cars or truck tankers. Loading is also controlled automatically from an isolated control room.

## 5. DESCRIPTION OF PROGRAMS

### 5.1 INDUSTRIAL HYGIENE

The safety and health program for the entire facility is headed by Mr. W H Meyer, Safety, Health, and Environmental Manager. The program is basically autonomous, with support provided by the company and corporate office. The chemical plant has a management safety committee that consists of the plant manager as chairman, the safety superintendent, and other managers and superintendents. The committee covers all aspects of the safety and health program. Safety meetings for the workers are conducted monthly. These meetings are conducted by operations supervision with direction and input from the safety department.

Mr. G. Ille, plant industrial hygienist, coordinates the industrial hygiene program for the Bishop plant. Industrial hygiene monitoring and analysis is performed by a technician and chemist under the direction of Mr. Ille. Personal long- and short-term samples, and some general area samples, have been taken for many air contaminants, including formaldehyde and methanol. A "Formaldehyde Task Force" was established to determine the formaldehyde exposure for each job classification, within an exposure zone, with the objective of reducing employee exposure to formaldehyde. All employees are informed of sampling data results and interpretation of results in writing from the plant industrial hygienist.

The Company and Plant industrial hygiene staff initiated a "Health Surveillance System" in 1977, which is integrating the following four health program factors:

- health history of employees,
- inventory of chemicals,
- duration of exposure,
- level of exposure

The Company industrial hygiene staff has set internal permissible exposure limits (PEL) for toxic air contaminants where recommended PEL's already exist.

Contingency plans for emergencies are well defined. The Bishop plant has its own firefighting crew. The plant has a written emergency spill control program, and all employees are trained using an in-plant training film.

## 5.2 OCCUPATIONAL SAFETY AND HEALTH (OSH) TRAINING

A training coordinator manages the employee training program. The plant uses a process simulator for training that can simulate several basic processes in the plant. The plant has produced its own safety and health training films that are shown to new and existing employees, and these films are presented to new employees on a scheduled basis. The new employee training program consists of training in various modules, such as safety, health, environmental problems, spill control, etc

Employees are advanced from less responsible positions to those of more responsibility over a period of time so that the employee is adequately trained on the job in all aspects. An employee works 3-4 years as a helper before becoming an operator.

## 5.3 PERSONAL PROTECTIVE EQUIPMENT (PPE) AND SAFETY EQUIPMENT

All employees working in the formaldehyde production area are required to wear safety glasses and hard hats. The plant has a written respiratory protection program, managed by the plant

industrial hygienist and the Safety Superintendent. Respirators are maintained at a central location. When respirators are in need of cleaning or repair, they are sent to this location for an exchange. The plant industrial hygienist is now in the process of developing a quantitative fit testing program using Freon 12. Cartridge respirators, which are currently used for formaldehyde exposures, are half- and full-face and are approved for an organic vapor/acid gas exposure.

For any noise exposure greater than 85 dBA, Celanese requires the wearing of ear protection. The Company and Plant industrial hygiene staff is now determining which type of ear protection is acceptable by the majority of employees, based upon wearing comfort. This is being done so that employees will wear hearing protection of their own accord where required.

Emergency eye washes and showers are located along the tank truck and rail car formaldehyde loading racks. One or more eyewashes and showers are located at each MO unit and are also located at the central formaldehyde storage and blending area. In addition to a hard hat and safety glasses, PPE required for specific operations is as follows:

Loading Operations (while on the loading rack or tank truck or rail car)

- Full- or half-face cartridge respirator
- Safety goggles, if half-face cartridge respirator worn
- Gloves (when withdrawing sample)

Paraformaldehyde Cleanout form Formaldehyde Storage Tanks Through Entry

- Air-supplied respirator
- Gloves, rubber
- Boots, rubber
- Protective full-body suit

Changing Catalyst in Reactors

Full-face cartridge respirator  
Gloves, rubber  
"Tyvec" overalls

Formaldehyde Storage/Load Tank Sample Withdrawal

Full- or half-face cartridge respirator  
Gloves, rubber

Maintenance-Formaldehyde or Methanol Major Leak Repair

Full-face cartridge respirator  
Gloves, rubber

5.4 MEDICAL PROGRAM

The Bishop plant employs a full-time nurse. An extensive physical examination is given to all employees every one, two, or three years, based on the employee's age. No specialty examinations are given to employees working at the formaldehyde production facility.

An audiometric test is given to those employees who are exposed to noise at an exposure equal to or greater than 80 dBA.

## 6 WORK PRACTICES

### 6.1 GENERAL PROCEDURES

#### 6.1.1 Operators

One operator is assigned per shift to each MO unit. An extra operator is assigned to fill in on duties as needed over the four shifts. The operator is responsible for operation of his specific MO unit and spends the majority of his work time (approximately 6 hours) within the MO control building, either operating controls for the unit or analyzing formaldehyde process samples taken to monitor the process. The operator also usually eats lunch within the control room as part of his shift. The operator for the MO-2 unit is also required to operate controls for a nearby boiler house, from the MO-2 control building.

The operator leaves the control building every four hours to collect formaldehyde process samples from the distillation column (two points; overhead and residue) and the absorber, and water samples from the boiler house. The operator also leaves the control building twice per shift to gauge tanks. During gauging, the operator checks the process equipment and pumps for detectable leaks. If a major leak is detected in the unit, the operator is to report it to maintenance unless he can easily repair it by himself. The operator may leave the control building to assist a maintenance worker repairing the leak.

### 6.1.2 Maintenance

Approximately 120 maintenance workers are employed by the plant, and service the chemical plant units. They are assigned to the day shifts only, but may work on other shifts for major emergency repair work.

Maintenance workers may repair all types of equipment, including chemical leaks of all kinds. The plant has spare pumps available to replace most of the pumps in the plant. If a pump breaks down in the field, it is replaced with a spare if one is available. Replacement procedure includes first closing off the pump from the rest of the system and then flushing out the isolated line and pump with deionized water from an enclosed deionized water system. The system is either flushed within enclosed piping to the underground sewer, or flushed waste is directed on the surface to a sump. Once flushing is complete, the malfunctioning pump is removed and replaced with the spare. The bad pump is then taken back to the maintenance shop for repair. The entire replacement procedure takes approximately 30 minutes. Since less work is done in the field where there are no ventilation facilities, the worker's exposure should be less than if the pump was totally repaired in the field. If a spare pump is not available, the pump is repaired in the field, which on the average, takes approximately two hours. The same isolation and flushing procedure is used for flushing the isolated line and pump with deionized water if the pump is repaired in the field.

As stated in Section 6.1.1, the operator checks pumps twice per shift for leaks when gauging tanks and report leaks to maintenance for repair. The plant does try to maintain a yearly turnaround maintenance program for each MO unit.

In addition to equipment repair, maintenance workers also change reactor catalysts and clean paraformaldehyde formations within formaldehyde storage tanks when needed.

## 6.2 FORMALDEHYDE LOADING

### 6 2.1 Blender Operator Duties

The blender operator spends approximately 80% of his time in a separate blend control room located adjacent to the rail car loading area. The blender operator works only the first shift. The operator transfers formaldehyde solution from two large storage tanks to six holding tanks, by using the control panel within the blending control room. The operator then automatically transfers formaldehyde from one or more holding tanks to tank trucks or rail cars through use of the control panel. The correct formaldehyde solution concentration is obtained by inline blending within the line feeding either the truck or the rail car. The operator does occasionally leave the building to read level gauges on holding tanks, turn valves on tanks to transfer solution from one tank to another, or collect holding tank samples. The procedure used to collect samples will be described in Section 6.3.

### 6.2.2 Truck Tank Loading

Truck tanks are loaded only during the first shift. The loading operator works along an elevated loading rack which is equipped with three formaldehyde loading stations; normally only two are used.

After a truck pulls up along the rack, the operator puts on a respirator and opens the hatch to ensure that the truck is empty. He then connects a flexible air displacement duct and the loading line to the truck. The air displacement duct is connected to the vent systems which, includes a packed scrubber. The loading line

enters the truck through the top hatch and extends down almost to the bottom of the tank. A level gauge probe is also inserted into the truck. Prior to connecting the loading line to the truck, it is released from piping, where it is stored overnight. Residual water falls out of the line after releasing it from the piping. This water is remaining from a water flush of the loading lines, which is performed every day at the end of the first shift. Residual formaldehyde remaining in the lines is flushed from the enclosed system to the sewer. The exposure due to residual water falling out of the line should be minimal, since very little, if any formaldehyde remains in the line.

Once all lines are connected to the truck, the hatch is closed, and the loading line is flushed with air prior to loading. The amount of formaldehyde loaded is automatically controlled using a computer terminal located within the blending control building. After the tank is loaded, the line is flushed with air, the loading line and air displacement duct (vent line) are disconnected (as shown in Figures 3 and 4), and the depth gauge probe is removed. When the loading line is removed, up to two gallons of formaldehyde remaining in the flexible part of the line falls out of it to the ground 8 feet below the rack, creating a potential exposure to the operator.

The operator then opens the hatch to collect a sample, obtains the solution temperature, and checks the depth of the solution within the tank. A pint glass jar is used to collect a sample. Sample collection will be described in Section 6.3. The solution temperature is obtained by manually dropping a thermometer on a rope through the hatch opening. The depth of the solution is checked by inserting a wooden depth gauge into the filled tank.



Figure 3. Tank truck loading operator removing vent line from tank truck.



Figure 4 Tank truck loading operator removing loading dip tube from tank truck.

Once all tests are performed, all material which has been immersed in the formaldehyde solution, including the loading line, is hosed off with water as shown in Figure 5. In addition, all other contaminated areas, including the ground below the rack, are hosed off, and the effluent is discharged to the facility biological treatment plant.

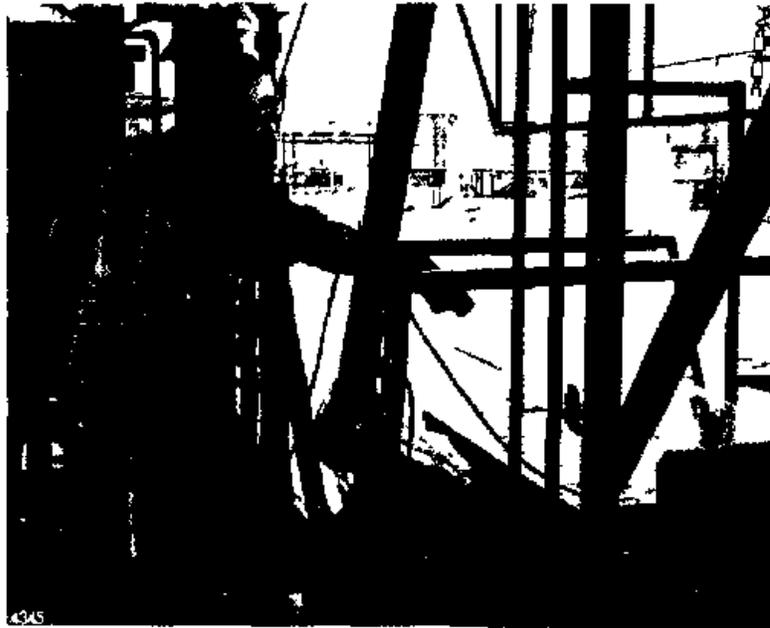


Figure 5. Tank truck loading operator hosing the tank truck off. Note respirator and gloves. Safety eyewash and shower behind operator.

### 6.2.3 Rail Car Loading

Rail cars are only loaded during the first shift. Rail cars are loaded from one of two loading racks located adjacent to the tracks.

Each rail car is equipped with two domes. One dome is retrofitted with attachments for the loading line, air displacement duct, and an opening for the depth gauge probe. The air displacement duct goes to the vent system, which includes a packed scrubber. The

operator hooks up the loading line, air displacement duct, and inserts the depth gauge probe, then loading commences. The other dome is normally closed.

Presently, because automatic loading of cars is not accurate due to problems with the computer controls, the operator must check the level of solution prior to completion of loading by opening the second (free) dome and visually checking the level as shown in Figure 6. This checking, which takes two to four minutes, is usually done only once while filling the rail car. The operator wears a respirator while checking the level. The status of the level is visually communicated to the blending operator. During this check, displaced contaminated air escapes from the dome and may be blown towards the operator's breathing zone, depending upon the direction that the wind is blowing.

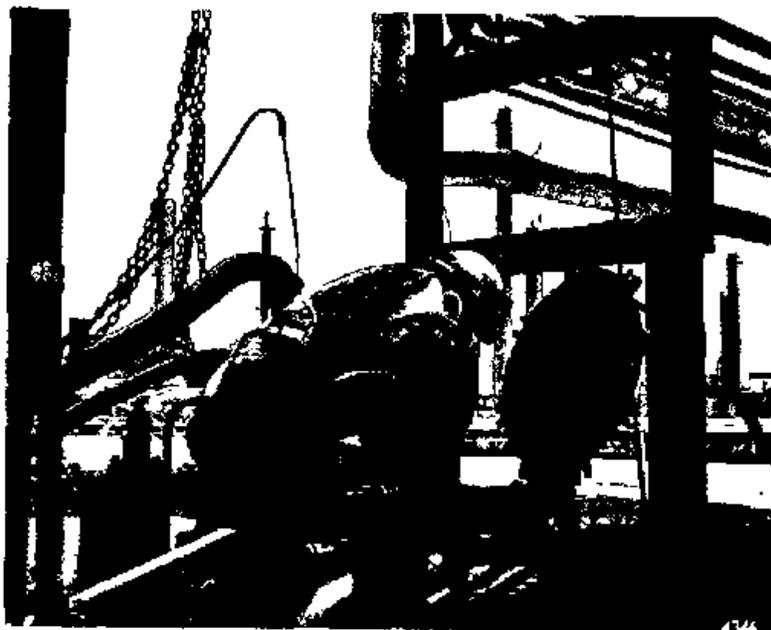


Figure 6 Rail car loading operator checking tank level. Note respirator.

When loading is complete, the operator collects two samples (each one pint, in a glass jar) through the free opened dome. The specifics of a collection are described in Section 6.3. Also, a thermometer attached to a rope is lowered into the tank to obtain the solution temperature. The loading line, air displacement duct, and depth gauge probe are removed from the car (Figure 7). The open dome is closed. The loading line is then flushed with air. Once these tasks are completed, the closed samples and all other materials contaminated with formaldehyde are hosed off with water, the effluent going to the facility biological treatment plant. In addition, the contaminated rail car top is hosed off.



Figure 7. Rail car loading operator removing loading line from tank car. Note respirator and gloves.

### 6.3 FORMALDEHYDE SOLUTION SAMPLE WITHDRAWAL AND ANALYSIS

#### 6.3.1 Formaldehyde Process Samples

The unit operator takes a process sample from the absorber, the lower section of the distillation column, and the overhead from

the distillation column, twice per shift. The samples are usually taken at four-hour intervals (4, 8, and 12 o'clock) throughout the three shifts.

Initially, the unit operator fills two flasks with 100 mL of water and three flasks with 100 mL of sodium sulfite while in the unit control building. The operator then transports pint glass jars to the unit sample points and collects each of the samples in one of the glass jars. Samples are taken by opening a ball valve and filling the jar through tubing from the sample point. A catch basin is provided below each sample point. The operator purges the system (Figure 8) prior to filling and dumps the purge into the catch basin. The catch basin directs waste to the sewer.

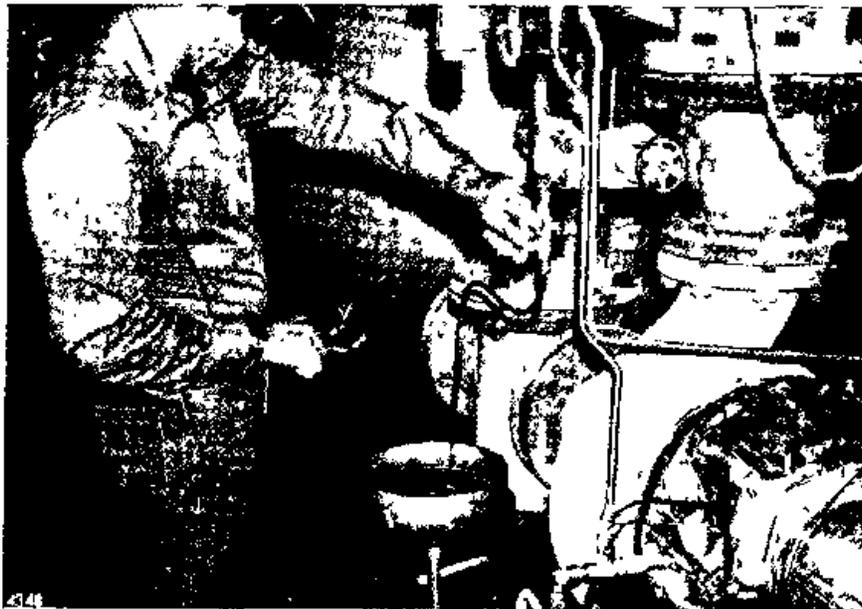


Figure 8. Unit operator purging absorber recycle line prior to sampling. Note catch basin, sample tongs, and splash goggles.

The operator did not wear a respirator while taking samples. Since the pint sample bottles are capped and they are outside of a hood only about five minutes, respiratory protection may not be needed

Once a jar is filled (Figure 9) it is covered with a screw top (Figure 10). The three filled jars are then taken back to the control building and placed within a local exhaust-ventilated laboratory hood. Three small vials are each filled within the lab hood, with sample solutions taken from each of the three sample points. Each vial is weighed on a balance located outside the hood. This should present a minimal exposure due to the small quantity being weighed. The formaldehyde from each vial is dumped in one of the flasks containing 100 mL of sodium sulfite and titrated with sulfuric acid (Figure 11) within the hood to determine the percent formaldehyde within the samples taken from each of the three sample points.



Figure 9. Unit operator sampling process.

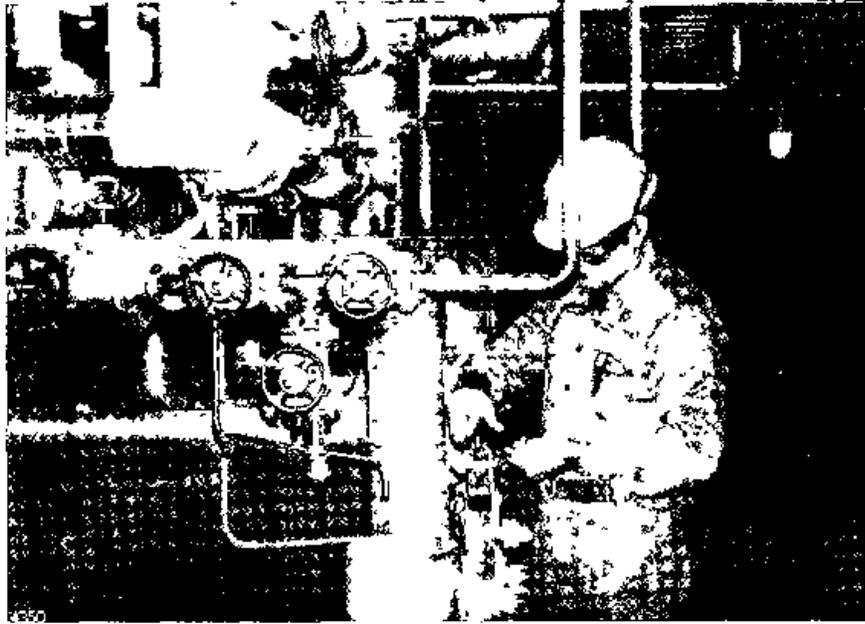


Figure 10. Unit operator capping process sample.

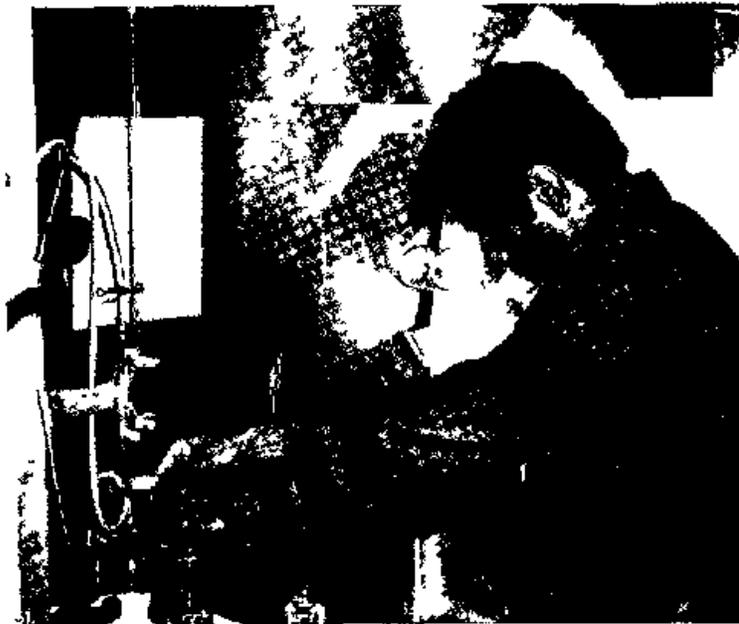


Figure 11. Operator analyzing samples in the local exhaust hood.

A portion of the absorber sample is pipetted from the jar to one of the two flasks containing 100 mL of water. The flask solution is titrated with sodium hydroxide to determine percent formic acid. The entire task is performed within the lab hood. This procedure is repeated for the sample taken from the lower section of the distillation column.

A sample from the jar containing the sample of the overhead from the distillation column is drawn into a syringe. This is performed within the lab hood. Approximately 4-5 mL from the syringe are injected into a gas chromatograph (GC) (Figure 12) located outside the hood. A standard is then injected into the GC. The percent methanol is then determined. The formaldehyde exposure due to injection of the sample should be low since the sample contains mostly methanol.



Figure 12. Operator injecting methanol sample into GC. Note hood on left side.

After all analyses are performed, the flasks and glassware are washed within the hood. All waste is dumped into a sink within the hood, which directs waste to the plant's waste treatment facility

### 6.3.2 Loading Sampling

A loader operator withdraws a formaldehyde sample from each rail car or tank truck after it has been loaded. After a tank truck is loaded, all lines are disconnected. The hatch is opened and a sample is collected by lowering a pint glass jar, either held at the end of a long pole or at the end of a chain, into the solution to fill it (Figure 13). The jar is then removed and closed with a screw-type top.



Figure 13. Tank truck loading operator sampling tank truck. Note handle, gloves, and respirator.

The loader operator takes rail car samples by consecutively lowering two, one-pint glass jars on the end of a chain into the solution through the free dome. Once each is filled, it is removed and covered with a screw-type top. The operator always wore a respirator while the hatch was open for sample taking.

Both tank truck and rail car samples are then transported by vehicle to the main laboratory for analysis. Since the loader operator must open the hatch or dome to collect a sample, he may be exposed to formaldehyde gas escaping the tank truck or rail car. Since loading has ceased prior to sample collection, the exposure should be less than when the loader operator opens the dome on a rail car prior to completion of loading. During this latter task, displaced air is being forced out of the rail car due to loading.

The blender operator also occasionally withdraws samples from load tanks so as to double-check the formaldehyde concentration loaded into rail cars or tank trucks. The sample is collected in the same manner as process samples are collected by unit operators. A pint glass jar is filled with solution from a tank by opening a ball valve, which directs solution through tubing to the jar. The line is purged. Waste is dumped into a catch basin below each sample point, which directs the waste to the sewer. Once the jar is filled, it is covered with a screw-type top. The jar is then transported by another employee by vehicle to the main laboratory for analysis.

Samples are also collected every morning from the formaldehyde storage tanks by an MO-4 unit operator. Samples are collected in the exact manner as process samples are collected by unit operators. Purges are dumped in a catch basin below the sample point, which directs waste to the sewer. Samples are transported to the

main laboratory for analysis by laboratory technicians. The sampling team was unable to take personal samples on an employee while collecting these samples since its members were always busy collecting other samples at the times they were taken.

## 7. CONTROL STRATEGY

Several areas of the formaldehyde production operation that present exposure potential are discussed below with respect to control technology applied. This discussion is limited to one of the four methanol oxidation units, and the common storage and shipping areas found at the plant. This limitation was accepted because the operations are similar, time and cost restrictions on the project made it impossible to do all four units simultaneously, and the plant personnel requested that the sampling be restricted to this area

Exposures are limited because the process is completely enclosed, except for the formaldehyde discharge (loading) point, and process sample points. This enclosure includes the methanol raw material to be oxidized. Methanol is piped to the storage tanks for use by the unit.

### 7.1 MO-2 METHANOL STORAGE AREA

Methanol is produced at the Bishop plant and stored for use in formaldehyde production in two storage tanks, approximately 75 feet from the MO-2 reactors. The large floating roof tank and the smaller fixed roof tank shown in Figure 14, are grounded, diked, and equipped with Varec level-indicating gauges. Methanol is pumped from the tanks, alternately emptying one while the other is filling, using a small centrifugal pump (Figure 15), with a Durham single mechanical metallic seal. Methanol from the pressure side of the pump is returned to the seal to lubricate the seal face. Methanol was noticed dripping from the working pump during source sampling. A second parallel pump, shown in Figure 16, is available should the primary pump fail.



Figure 14. MO-2 methanol storage tanks.  
Note dike around both tanks.

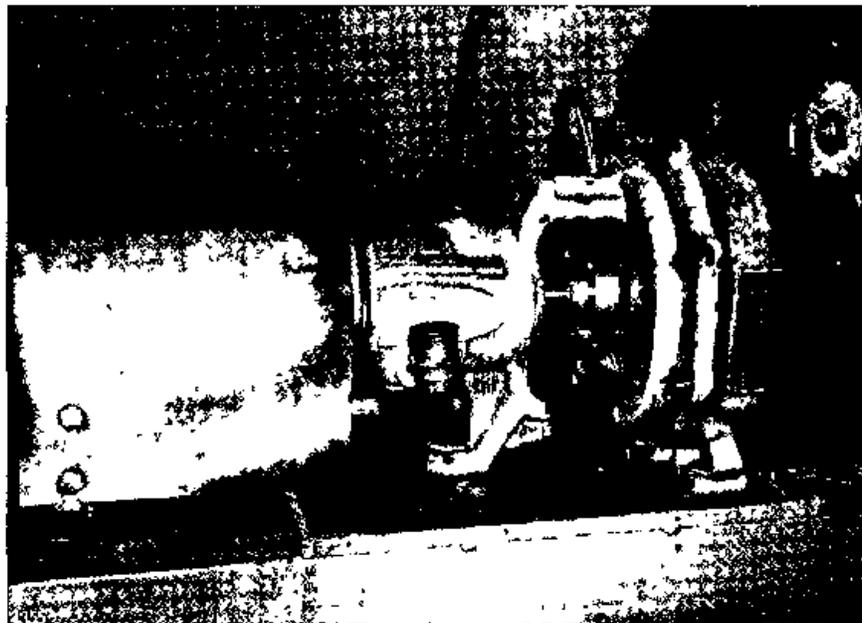


Figure 15. Methanol transfer pump.



Figure 16. Methanol transfer pumps inside diked area.

Methanol is pumped from the storage tanks through an enclosed cartridge filter, to the vaporizer, where it is combined with recycle methanol from the distillation column.

#### 7 2 MO-2 CONVERTER AREA

Two banks of converters are side-by-side in an open air, roofed structure. These converter banks, which are each made up of small reactors, are enclosed systems using fiber gaskets on each reactor end to prevent leaks. Each individual reactor is attached to a vaporized-methanol manifold and to a product manifold via a flexible pipe. The product manifolds are joined and then connected to a heat exchanger and then to the absorber. Cooling of the reactors is accomplished via natural convection. The nature of the enclosed process makes additional controls in this area unnecessary as long as the process is monitored for leaks. One reactor did have a vapor leak through one gasket during the first part of the survey. The leak was repaired by an operator and checked later by maintenance personnel.

### 7.3 ABSORBER AND DISTILLATION COLUMN

Hot product gas leaving the converters is cooled in a heat exchanger and then enters the absorber, shown in Figure 17, where it is quenched with an aqueous formaldehyde solution. Exhausted gas from the top of the absorber, containing hydrogen, carbon dioxide, nitrogen, and small quantities of formaldehyde, is sent to a nearby boiler where it is burned to recover the heating value.



Figure 17. Absorber (right) and distillation column. Note exhaust line downstream of absorber.

Durco centrifugal pumps transfer the solution to three levels inside the absorber column. The pumps that transfer solution to the top and middle levels use Durham metallic single mechanical seals with recycled solution on the face of the seals. This recycle helps to lubricate the seal, improving its effectiveness and longevity according to the manufacturer. The bottom recycle pump, shown in Figure 18, uses a Chesterton tandem, double mechanical seal with methylene glycol on the seal for lubrication and sealing.

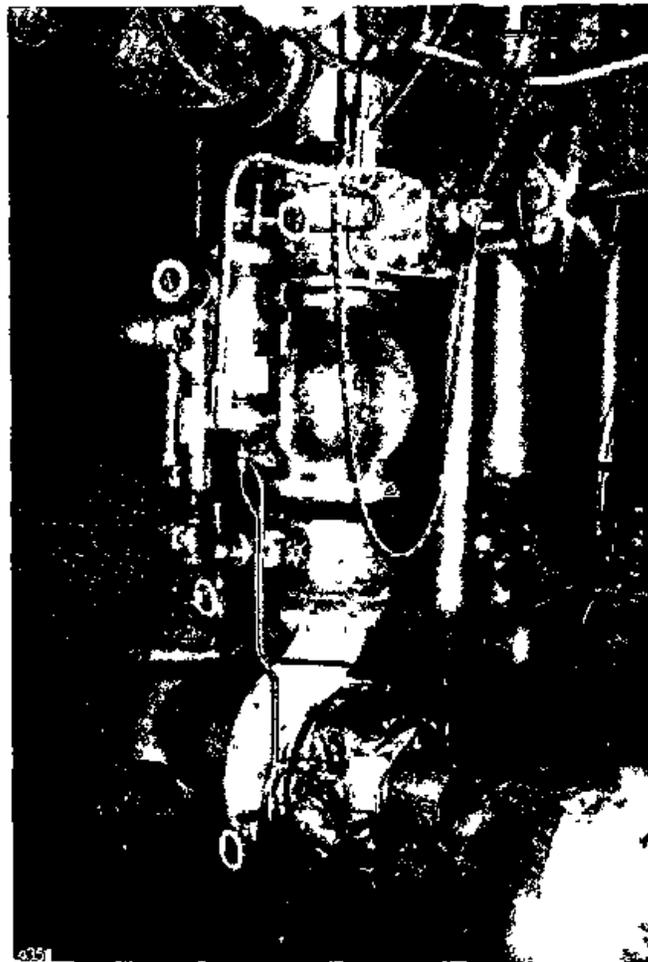


Figure 18. Bottom recycle pump. Note double mechanical seal vessel and lines. Note sample point on left.

Double mechanical seals appear to offer several potential advantages over single mechanical seals. For example, leaks must pass through two seals before they are emitted to the atmosphere. In addition, leaks can be detected earlier by contamination of the sealing fluid by the process solution or by a lowering of the sealing fluid level in the fluid supply vessel. Twenty double mechanical seals have been installed at the Celanese plant. However, evaluation of double mechanical versus single mechanical seals has just begun. No conclusions have been made yet.

The distillation column uses similar pumps having double mechanical seals to transfer the interim solution to the column and the product solution to the product tanks. A centrifugal single mechanical seal pump is used to transfer the recovered methanol to the vaporizer for reuse, as shown in Figure 19.

#### 7.4 MO-2 PROCESS SAMPLING

Process samples are taken every four hours from four points on the product end of the process. Samples are taken from the absorber lower recycle pump (Figure 18), the distillation product pump (Figure 20), the distillation methanol recycle pump (Figure 19), and from the final product line (Figure 21). Each sampling point is a short line off of the pressure side of the respective pump, which has been fitted with a small gate valve, a pressure indicator, and a small ball valve. Each sample point also has a small catch basin for purging the line and collecting drips from the sample points. These catch basins empty into the plant central sewer system, where the purged material is then treated by the plant. All sample points and catch basins are out of the breathing zone and are readily accessible. Operators wear safety glasses and use beaker tongs during sampling to reduce accidental eye and skin contact. An eyewash and safety shower are within 25 feet of all sample points.

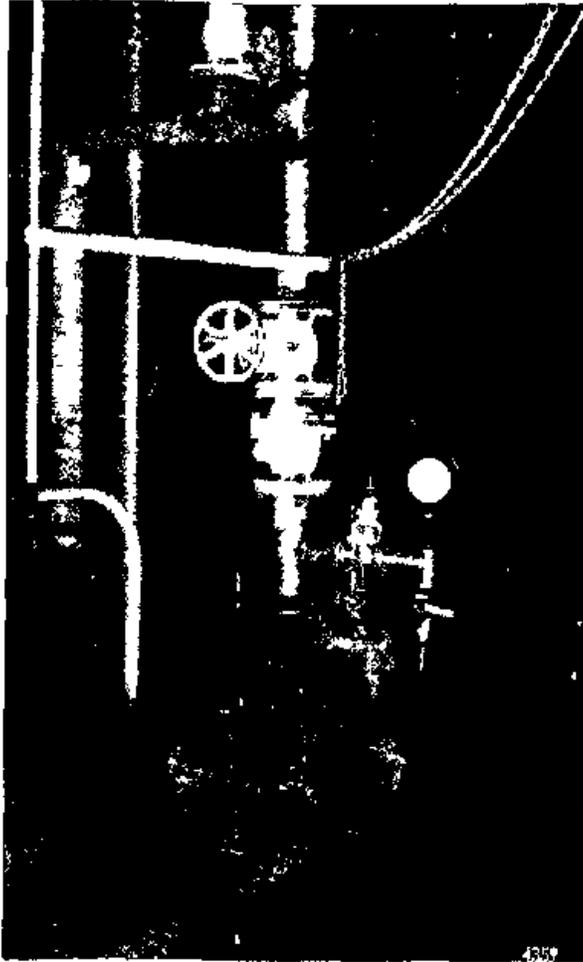


Figure 19. Methanol recycle pump from distillation column. Note sample point and catch basin.

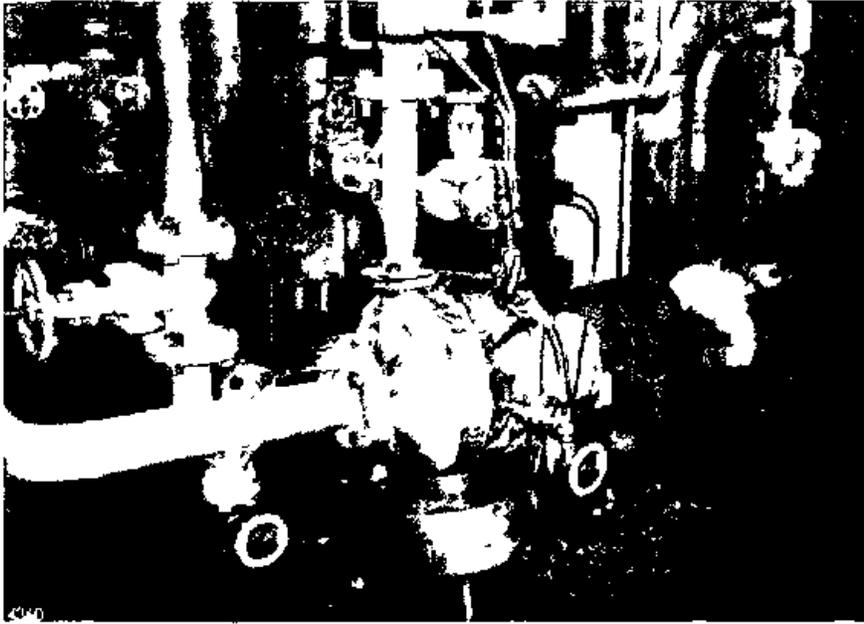


Figure 20. Distillation product pump point.  
Note catch basin.

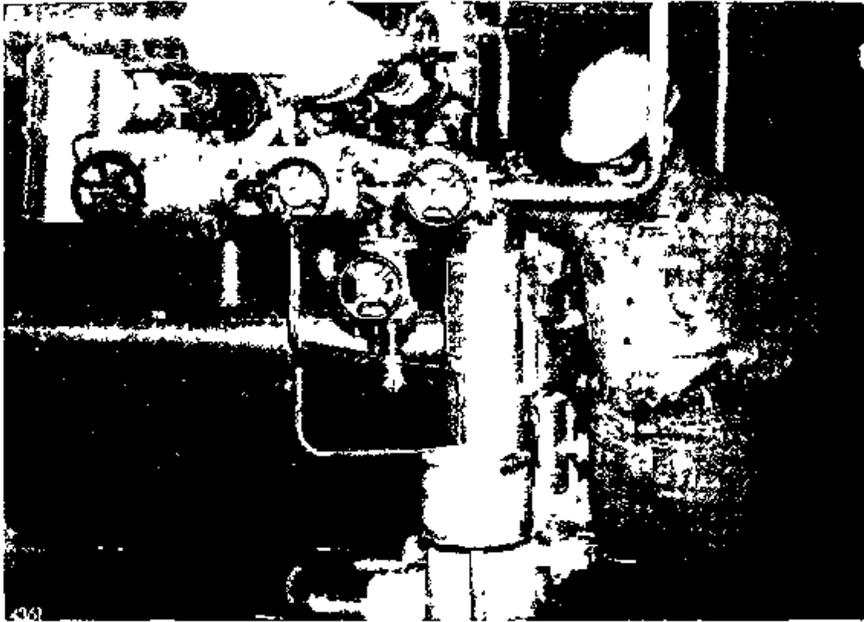


Figure 21. Final product sample point.

## 7.5 CENTRAL FORMALDEHYDE STORAGE

Formaldehyde produced by the MO-2 unit is pumped to large storage tanks near the loading area of the plant. This area also stores the formaldehyde produced by the other units that are not used by the plant. The storage area surveyed consisted of four, one-million gallon tanks. Each tank is grounded, has Varec exterior level gauges, and has a small packed column water scrubber to capture any formaldehyde released by the tank. Each tank also uses an exterior heat exchanger to maintain the tank temperature at 60°C and prevent paraformaldehyde formation.

An example of the water scrubber used to control formaldehyde emissions from each tank is shown in Figure 22. A schematic of the scrubber is shown in Figure 23. Vapors can escape from the tank at any time, with the worst case occurring during tank filling. The gas above the formaldehyde solution can be assumed to be in equilibrium with the solution (50% solution at 60°C) and to contain a significant formaldehyde concentration. As the tank is filled, this gas is forced out of the tank and through the scrubber. The water used in the packed scrubber captures the released formaldehyde, forming a solution containing approximately 2 percent formaldehyde. The scrubber gas is then released to the atmosphere. The packing material (1/2-1 in. rings) increases the contact time and area of the scrubber, improving the percent capture. The scrubbers, designed for 95% efficiency, are in 24-hr operation and use approximately 0.25 gpm water. Samples of the scrubber effluent were analyzed for the Texas Air Quality Board and were found to contain very low formaldehyde concentrations in the released gas.

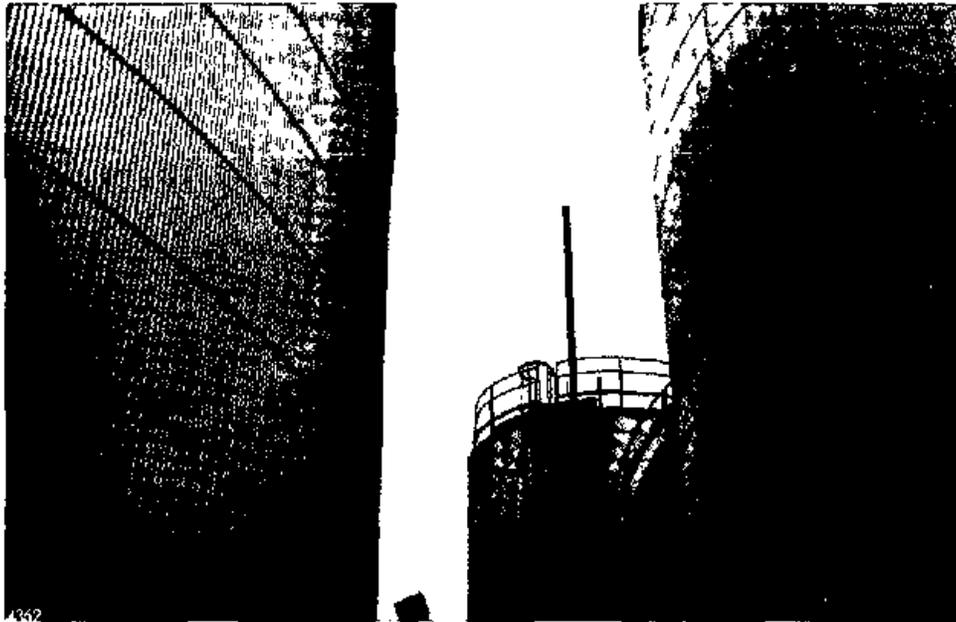


Figure 22. Formaldehyde storage tank scrubber (center) extending above tank.

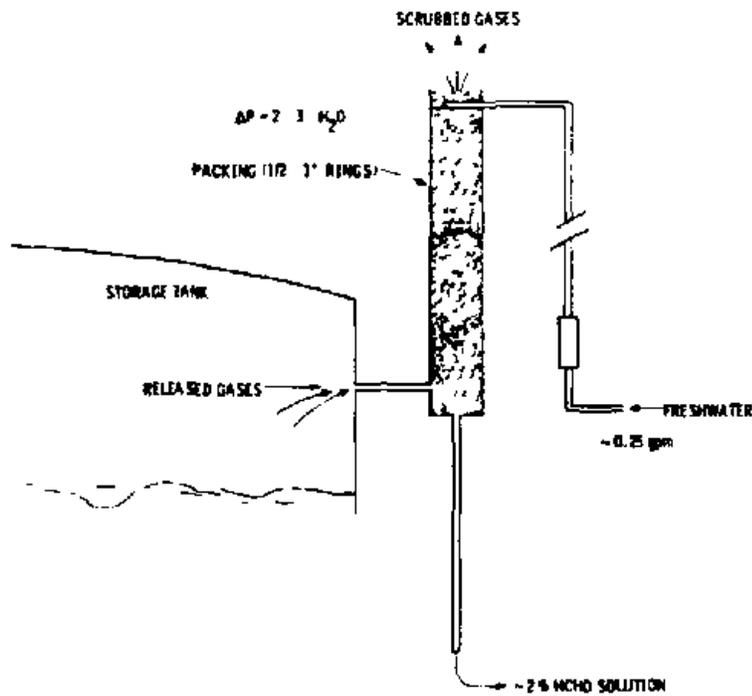


Figure 23. Schematic of packed scrubber on formaldehyde storage tanks.

The use of external heating systems on the storage tanks, to maintain the 60°C tank temperature, reduces the need for entering the tank. It also allows the plant to spot and correct maintenance problems since the flanges and fittings which are most likely to leak are exposed. The system uses centrifugal pumps with Chesterton tandem double mechanical seals to pull the formaldehyde solution from the tank, pump it through a shell-and-tube heat exchanger, and pump it back into the tank. Methylene glycol is used in the double mechanical seal to lubricate and help seal the seal faces. Each pump operates 24 hours per day. There is a sample point on the pressure side to allow the blender operator to determine blending requirements. Catch basins around each pump prevent major leaks from contaminating the entire area. Figures 24 and 25 show the pumps and the double mechanical seals used in this area.

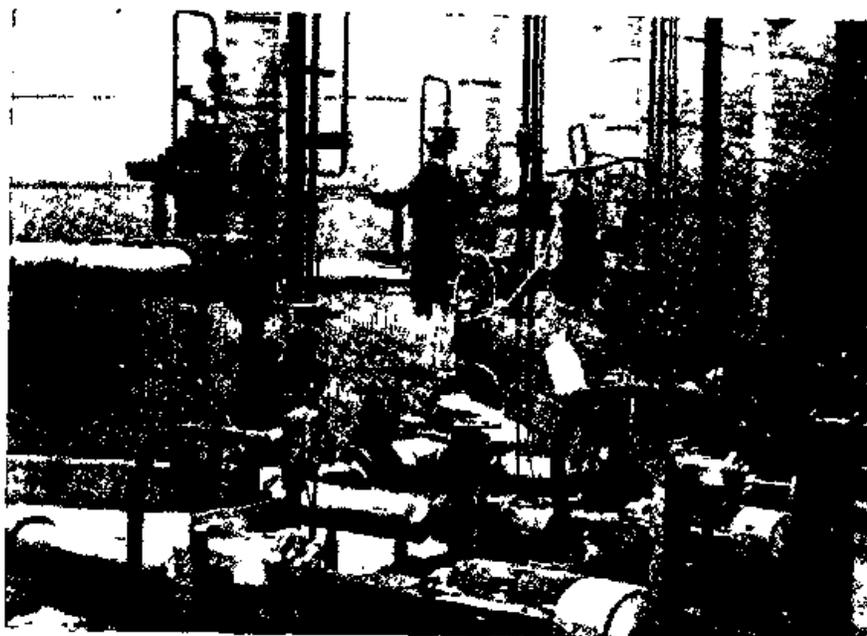


Figure 24. Storage tank recirculation pumps with double mechanical seals.

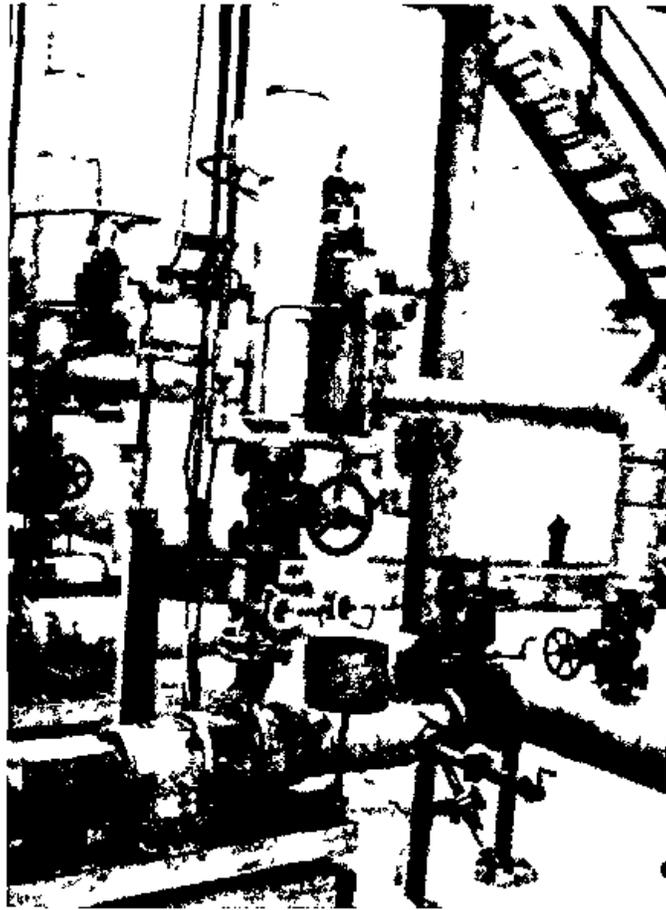


Figure 25. Double mechanical seal with sealing fluid vessel.

#### 7.6 FORMALDEHYDE LOADING AREA

Formaldehyde is loaded in two separate areas, one each for tank trucks and rail cars. These areas are adjacent to each other and use the same control equipment. Celanese owns the majority of the rail cars and tank trucks that transport formaldehyde from the plant and has modified each carrier to conform to a closed-top loading system. A closed liquid system is used to deliver the formaldehyde solution to the carrier, and a closed ventilation system is used to carry the released vapors to a central scrubber.

Tank cars carry most of the formaldehyde solution out of the plant. The tank car loading area, shown in Figure 26, is an elevated platform with several loading spots. Each spot has a set of flexible metal hoses (Figures 27 and 28), that can be attached directly to the tank car, shown in Figures 29 and 30.

Each set has one delivery hose and one ventilation hose. The ducts are fitted with gasketed quick-connect adapters for easy use. Product formaldehyde solution is pumped from the blending area into the tank through an enclosed system. The ventilation system is also enclosed and uses the natural pressure of the displaced air from the loading operation to push the vapors through a packed scrubber. This scrubber is similar but larger than those used on the formaldehyde storage tanks, but it is only in operation during loading activities.

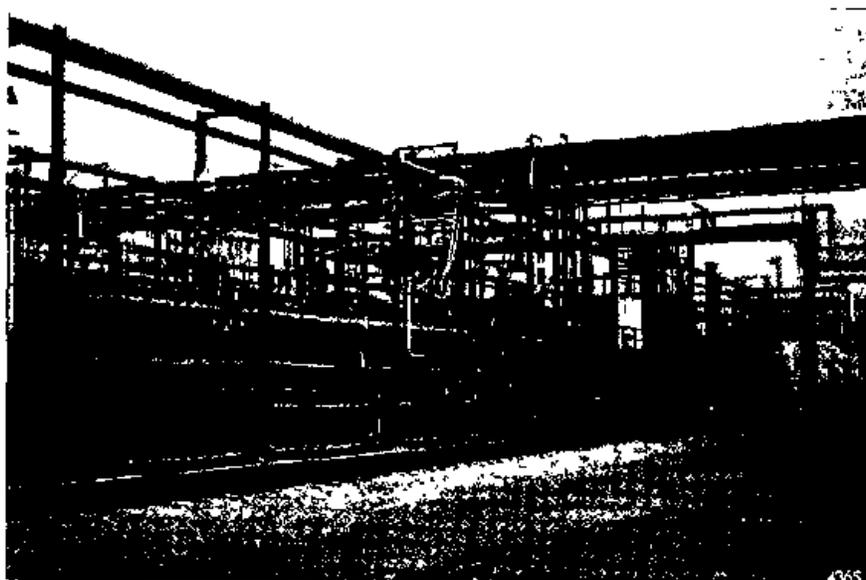


Figure 26. Tank car loading area.

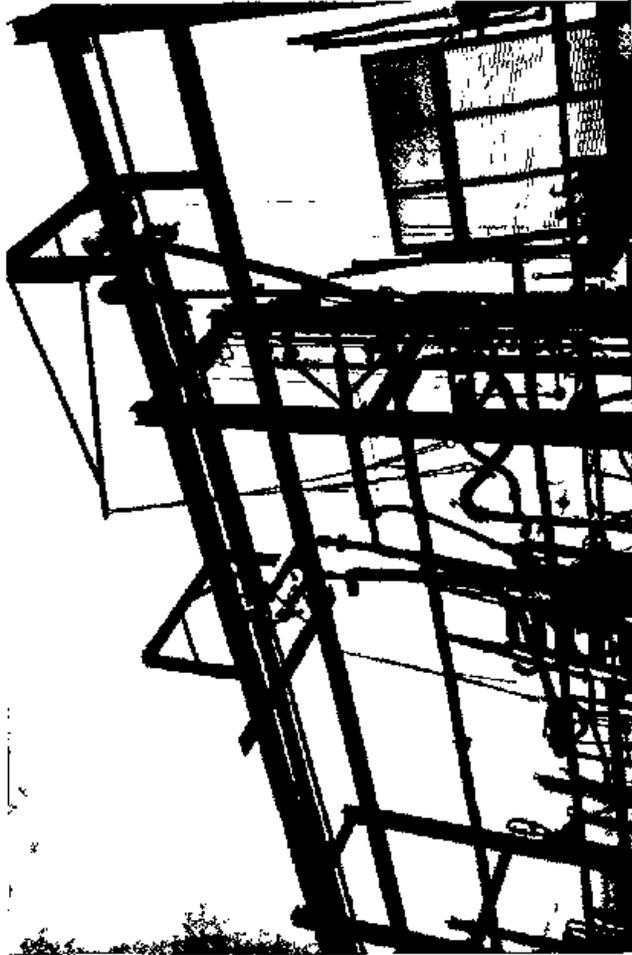


Figure 27. Loading and ventilation lines for tank car loading.  
Note flexible lines & storage position at left center.

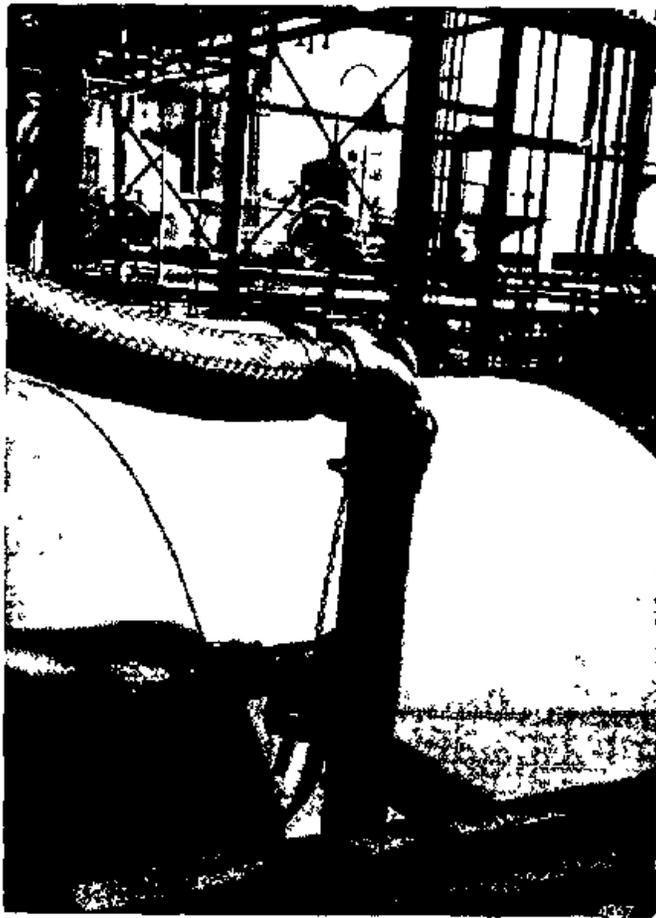


Figure 28. Storage position for loading and ventilation lines.



Figure 29. Loading and ventilation lines attached to tank car.

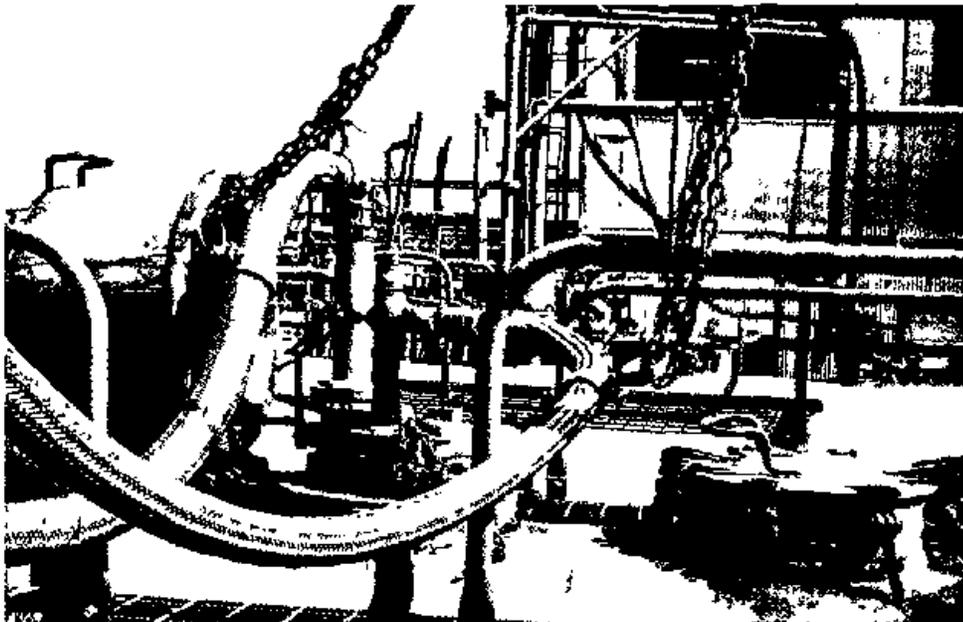


Figure 30. Close up of loading and ventilation lines hook-up.

At present, shipment samples are taken by hand from every tank that goes out of the plant, reducing the efficiency of this closed dome system. Efforts are being undertaken to resolve the problems with the automatic sampling system to eliminate the need for routinely opening the filled tanks. In addition to opening the tank car for sampling, the operator must also observe the final filling stages of the tank because the automatic loading system is not sensitive enough to prevent overfilling. Loading operators wear half-face cartridge respirators whenever the tank is open.

The truck loading area, shown in Figure 31, also has several bays where formaldehyde can be loaded. The same enclosed systems used for tank car loading are used, except that the modifications for truck loading are not completely permanent and require significantly more operator activity. For instance, the operator must manually insert a level indicator tube into the attachment on the second hatch. Figures 32 and 33 show a truck being loaded. Note the two flexible metal hoses attached to tank top. These connections are uncoupled prior to the truck leaving. Figure 4 shows the operator removing the loading dip tube from the tank. Figure 34 shows the adapter for the ventilation system. Both of these adapters have quick-connect fittings to minimize operator effort.

The loading and ventilation systems operate on the same systems used for tank car loading. Natural air pressure pushes the released vapors through the central scrubber. Unlike the rail car system, an accurate level indicator allows the truck to be completely enclosed during all loading activity. Sampling is done by the operator through the open truck hatch while wearing a half-face cartridge respirator. The hatch is open for about three minutes. Formaldehyde spills are washed into the sewer below the loading area after each truck is loaded.

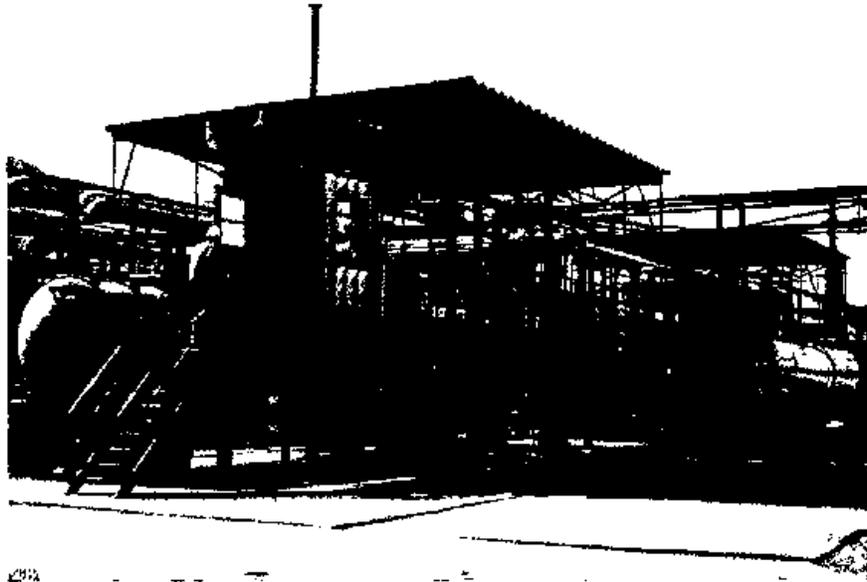


Figure 31. Tank truck loading area.

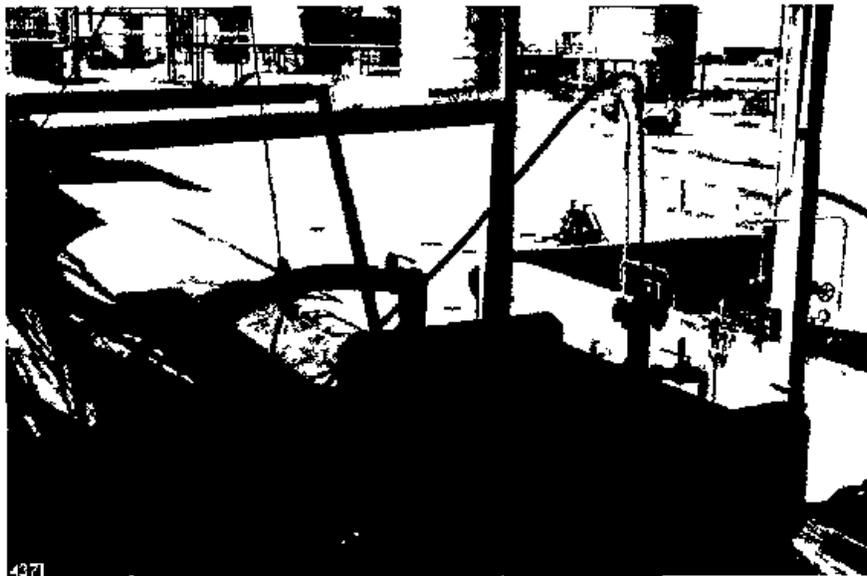


Figure 32. Tank truck with loading and ventilation lines hooked up. Note automatic level probe.



Figure 33. Tank truck with loading (right) and ventilation (left) lines hooked up.

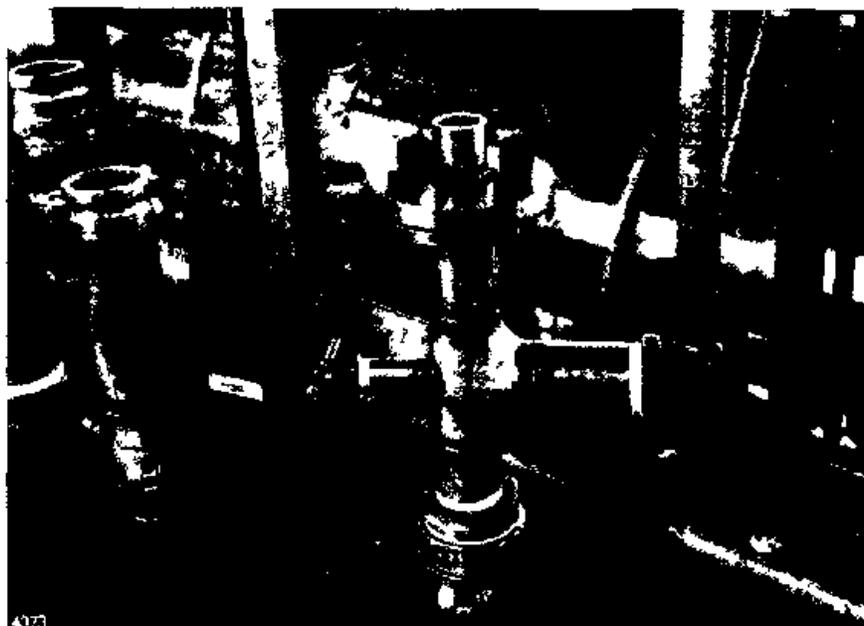


Figure 34. Celanese adapter for tank truck loading. Top line is for level probe, left is bleed valve, right is hook-up to vent line.

## 7.7 MO-2 CONTROL ROOM

Formaldehyde process operators spend most of their time monitoring the process area from the control room, which is located approximately 200 feet from the unit. Critical operations can be monitored and controlled from this area, and alarms warn the operator of problems as they occur.

Sample analyses for percent formaldehyde and formic acid in the samples collected from the process are conducted in a small hood in an ell of the control room. The lab hood is a compensating-type hood, with outside makeup air provided from a grill located along the top of the hood face. Inward air velocity measurements could not be made along the open hood face due to extreme turbulence at the face. Smoke tube air flow tests showed air being blown out of the hood, with some air movement upwards toward the exhaust plenum inside the face.

It is suspected that the reason for the undesirable flow patterns around the face of the lab hood is that more makeup air is being provided than is being exhausted. In fact, Celanese personnel measured the air velocity at the air makeup grill and found it to be 1,750 fpm. The hood was designed to deliver 400 fpm. Based upon the smoke tube air flow test, it is concluded that the hood was not operating properly and could not control formaldehyde gas produced during analyses performed within the hood. However, it would also be mentioned that this hood is rather new (less than one year old), and efforts were being made by Celanese personnel to balance the air flow across the hood face.

The injection of 4-5 mL of a sample of the overhead from the distillation column into the GC located outside the hood should produce a minimal formaldehyde gas exposure for the operator since the sample should contain mostly methanol and very little formaldehyde. No other operations within the control building should present a source of formaldehyde.

## 8. SAMPLING AND ANALYSIS

Formaldehyde and methanol sampling were conducted during the survey to determine time-weighted-average (TWA) and short-term exposure levels (STEL) for personnel and areas associated with formaldehyde production. Five process operators were monitored for formaldehyde exposure for one day. The breathing zones of two operators were sampled for methanol exposure for one and two days, respectively. Loading operators for the tank car and truck loading operations were sampled for formaldehyde for four and two days, respectively. The blending operator was sampled for four days. These samples were taken to determine the worker exposure during normal shift work. The process operators and maintenance personnel were also sampled during potentially high exposure activities for short-term exposure levels.

Twelve areas were also sampled for formaldehyde and methanol to determine general concentrations to which the workers are exposed in these areas. Four sources were sampled to estimate the contribution of these sources to the general formaldehyde and methanol concentrations. In order to ensure that the source samples represented the source emissions and were not affected by concentrations of the same pollutant in the surrounding area, or by dilution, each source sampled was wrapped tightly with clear plastic and tape-sealed as shown in Figure 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 were translated into the amount of pollutant released per day



Figure 35 Example of enclosure for source sample.  
Note sample tube inside plastic.

### 8.1 SAMPLING TIME

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

$$\text{TWA} = \frac{T_1 X_1 + T_2 X_2}{T_t} \quad \text{Ref. [1]}$$

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

This same formula was applied to personal as well as area samples. Long-term samples were repeated on a second day to enhance the survey results and to evaluate day-to-day variations in results.

Short-term samples were taken during operator activities that were expected to significantly contribute to and affect the results of long-term samples. The samples were also to indicate where controls may be most effective if the exposure concentration levels needed to be reduced. Short-term samples were taken at flow rates of about 200 cm<sup>3</sup>/min (as compared with 100 cm<sup>3</sup>/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 [2] and approved by the NIOSH project officer, Mr. W. N. McKinnery, Jr. The method uses sampling tubes packed with 2,4-Dinitro-phenylhydrazine (2,4-DNPH)-coated silica gel to absorb formaldehyde from the sampled gas. To draw the gas through the tubes, MRC used DuPont Model P200 portable sampling pumps set and calibrated to deliver a constant flow rate ( $\pm 5\%$ ) of approximately 100 cc/min (actual pumps ranged from 93.9-129.1 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 ( $\pm 5\%$ ) of approximately 200 cc/min (actual pumps ranged from 187.5-209.3 cc/min). Pumps were

checked for significant (greater than  $\pm 5\%$ ) deviation after use and the samples where a significant deviation was observed were discarded.

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 A

Sampling for methanol was conducted using a NIOSH-approved active dosimeter method, NIOSH S59. Silica gel tubes were used in conjunction with DuPont Model P200 pumps which were set and calibrated at a constant flow rate ( $\pm 5\%$ ) of approximately 50 cc/min (actual pumps varied between 45.6-59.4 cc/min) for personal, source, and area sampling. Pump flow rates were checked after sampling to ensure constant flow.

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

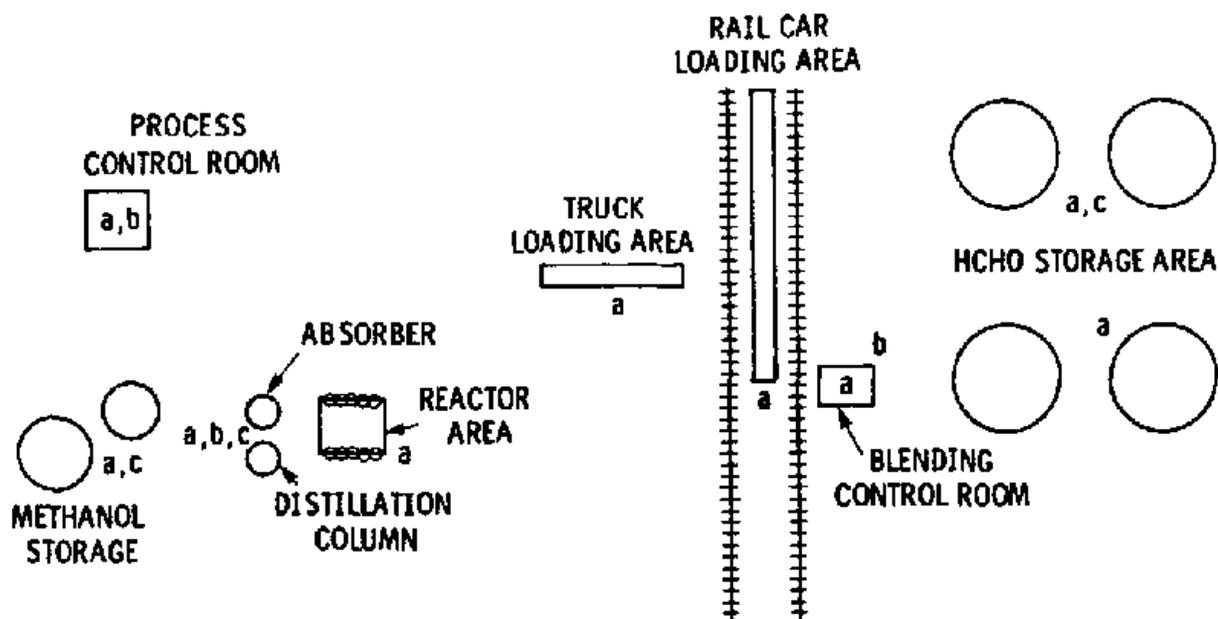
During sampling, a log of pertinent information was developed using Monsanto DMEH Industrial Hygiene Monitoring Forms. Recorded information on these forms includes: tube identification number, identification of sampling location, pump initial and final flows, sampling time, and comments.

### 8.3 NUMBER OF SAMPLES

Excluding blanks and spikes, 35 methanol samples were collected during the survey as shown in Table 1, Section 1.2.

### 8.4 LOCATIONS SAMPLED

Figure 36 shows the location in the plant where sampling was conducted. Table 2 lists the locations sampled and the number and type of samples taken at that location. Personal samples are not shown in Table 2.



- a - AREA SAMPLING
- b - SOURCE SAMPLING
- c - SHORT-TERM PERSONAL SAMPLING

Figure 36. Location of area, short-term personal, and source sampling conducted during the survey.

TABLE 2. AREA AND SOURCE SAMPLE NUMBER  
AND LOCATION SUMMARY

Location	Number of samples	
	Formaldehyde	Methanol
<u>Area</u>		
Converter - south side	4	3
Converter - center	3	3
Absorber	3	3
Distillation	4	4
Control room	4	
Formaldehyde storage - northwest	3	
Formaldehyde storage - southeast	3	
Methanol storage	3	3
Process sample analysis	5	
Truck loading	2	
Rail car loading	2	
Blending control room	2	
<u>Source</u>		
Distillation product pump	2	2
Absorber lower recycle pump	2	2
Formaldehyde recirculation pump	3	
Methanol supply pump		3

## 9. RESULTS

The following tables present the analytical results for samples taken at the Celanese Chemical Company, Inc., Bishop, TX, plant during October 11-15, 1982. All volumes and concentrations have been corrected to standard temperature and pressure (68°F and 29.92 in. Hg). Table 3 presents the long-term personal sample analytical results for methanol. No short-term methanol samples were taken. Area sample results for methanol are presented in Table 4. Source sample results for methanol can be found in Table 5.

Analysis of several of the methanol tubes showed breakthrough into the back section of greater than 25% of the quantity found on the front section. This indicates potentially significant loss of material and must be taken into account when comparing samples. Analytical results report these results as minimum values. These concentrations were doubled (i.e., assumed 100% breakthrough) when used to calculate the time-weighted average. The assumed values are reported in a separate column. The chemists who analyzed these samples agreed with this approach.

None of the sample results for formaldehyde are reported since the poor QC results indicate that their validity is open to serious question.

TABLE 3. METHANOL PERSONAL SAMPLE ANALYTICAL RESULTS

Description	Day	Shift	Tube number	Flow rate <sup>a</sup> cc/min	Sample time, min	Adjusted <sup>b</sup> volume, L	Concentration, ppm	Consecutive sampling period, min	Assumed <sup>c</sup> concentration, ppm	8-hr TWA, Average, <sup>d</sup> ppm
Operator 1	10/13	1	29	53.3	140	7.19	BDL <sup>e</sup>			
	10/13	1	25	53.3	143	7.34	BDL			
	10/13	1	26	53.3	115	5.91	BDL	398		<1.0
Operator 2	10/12	2	15	49.2	210	10.05	BDL			
	10/12	2	20	49.2	198	9.48	>3.48	408	6.96	3.89
	10/14	2	45	49.7	165	8.17	5.04			
Maintenance worker 3	10/14	2	48	49.7	218	10.80	3.70	383		4.28
	10/15	1	51	45.6	16	0.71	>8.34		16.68	
Maintenance worker 4	10/15	1	52	59.3	15	0.87	BDL			

<sup>a</sup>Flow rate determined as follows: within ±5% deviation of calibration, assume initial flow rate, greater than ±5% deviation of calibration, average the flow rates

<sup>b</sup>Adjusted to standard conditions (68°F and 29.92 in Hg)

<sup>c</sup>Assumed concentration = 2 x concentration due to >25% breakthrough

<sup>d</sup>Average concentration =  $(V_1C_1 + V_2C_2 + \dots) / (V_1 + V_2 + \dots)$

<sup>e</sup>Below detectable limits, 1.0 ppm

TABLE 4. METHANOL AREA SAMPLE ANALYTICAL RESULTS

Description	Tube number	Flow rate, <sup>a</sup> cc/min	Sample time, min	Adjusted <sup>b</sup> volume, L	Concentration, ppm	Assumed <sup>c</sup> concentration, ppm	Area <sup>d</sup> average, ppm
Converter area, south side of reactors (downwind), BZH, temperature is 30°C	03	50 0	244	11.85	Lost on desorption		
	05	50 0	225	10.93	>62 78	125 6	
	36	49 8	247	12 06	18 46	36.92	79.06
Converter area, center of reactors, BZH, temperature is 40°C	04	VOID					
	06	VOID					
	37	46 7	241	11.03	>12 08	24 16	24 16
Absorber area, downwind (SE) of middle recycle pump, BZH	02	50 0	231	11 22	>2 68	5.36	
	07	50 0	160	7 77	>3 93	7 66	
	33	50 7	250	12.21	>3.39	6.78	6 54
Distillation area, downwind (SE) of pumps, BZH	01	50 0	233	11.31	>2 36	4.72	
	08	50 0	155	7.53	>2 60	5 20	
	34/34A	48.8	186	8.90	>10.64	21 28	
	30	51 1	180	8.86	>3.91	7.82	9.64
Methanol storage area, MO-2, between pumps, BZH	10	54.2	248	13 10	>1.04	2 08	
	14	54 2	185	9 77	BDL	<1 00	
	38	59 4	224	13 16	>1.70	3 40	<2 23

<sup>a</sup>Flow rate determined as follows: within ±5% deviation of calibration, assume initial flow rate; greater than ±5% deviation of calibration, average flow rates

<sup>b</sup>Adjusted to standard conditions (68°F and 29 92 in Hg).

<sup>c</sup>Assumed concentration = 2 x concentration due to 25% breakthrough

<sup>d</sup>Area average =  $(V_1C_1 + V_2C_2 + \dots) / (V_1 + V_2 + \dots)$

<sup>e</sup>Below detectable limits, 1 0 ppm

TABLE 5. METHANOL SOURCE SAMPLE ANALYTICAL RESULTS

Description	Tube number	Flow <sup>a</sup> rate, cc/min	Sample time, min	Adjusted <sup>b</sup> volume, L	Concentration, ppm	Average <sup>c</sup> concentration, ppm
Distillation column product pump, double mechanical seal	17	49.4	92	4.43	7.71	7.55
	21	49.4	138	6.64	7.45	
Absorber lower recycle pump, double mechanical seal	18	48.9	129	6.15	1.02	1.22
	23	48.9	82	3.91	1.54	
Methanol supply pump	46/46A	56.3	129	7.24	>5,666 <sup>d</sup> /126	14,200
	44/44A	56.3	133	7.46	>6,523 <sup>d</sup> /1,365 <sup>d</sup>	
	49/49A	48.0	114	5.33	>9,769 <sup>d</sup> /2,802 <sup>d</sup>	

<sup>a</sup>Flow rate determined as follows: within ±5% deviation of calibration, assume initial flow rate; greater than ±5% deviation of calibration, average flow rates.

<sup>b</sup>Adjusted to standard conditions (68°F and 29.92 in. Hg).

<sup>c</sup>Average concentration =  $(V_1C_1 + V_2C_2 + \dots)/(V_1 + V_2 + \dots)$ .

<sup>d</sup>Minimum values due to breakthrough.

## 10. CONCLUSIONS

### 10.1 METHANOL EXPOSURE

#### 10.1.1 Operator Long-Term Exposure

Consecutive personal long-term samples were taken for the MO-2 unit operator during the 10/13 day shift and the second shift of 10/12 and 10/14. Sample data are shown in Table 3, Section 9.

Sample No. 20, taken on 10/12, had excessive breakthrough. Even if one assumes 100% breakthrough out of the tube with a resultant tube concentration of 6.96 ppm, the TWA exposure concentration for the total sample period of two samples worn on 10/12 is only 3.89 ppm. The TWA concentration for the set of samples taken on 10/12 was below the detection limit of 1.0 ppm and on 10/14 it was 4.28 ppm. All TWA exposure concentrations are greatly below the OSHA TWA PEL of 200 ppm. It is felt that the TWA exposure concentration gives a good estimate of the unit operator's exposure for the full shift worked. It can thus be concluded that the methanol exposure was controlled and nonexcessive for those days sampled. The exposure is most probably nonexcessive under normal conditions and will remain nonexcessive in the future if the operations remain similar.

#### 10.1.2 Maintenance Personnel Long-Term Exposure

Long-term personal samples could not be taken on maintenance workers since they provide maintenance over the entire plant complex. The maintenance workers did not spend a full shift in the formaldehyde plant area during the time the sampling team was on

site. The sampling team was able to take short-term personal samples on two maintenance mechanics changing filters on an MO-2 unit methanol pump. The sample data appear in Table 3, Section 9.

The concentration for one sample was below detectable limits whereas excessive breakthrough occurred in the other sample (No. 51). Even if 100% breakthrough is assumed and the reported result of 8.34 is doubled to 16.68 ppm, the exposure is still considered low.

OSHA does not enforce a short-term exposure limit (STEL). The American Conference of Governmental Industrial Hygienists recommends a STEL for methanol of 250 ppm. Both workers were exposed to a much smaller concentration, and thus the exposure is well below the accepted limit. It is also expected that maintenance workers should not regularly be exposed to excessive methanol over an entire shift. Their long-term exposures are most probably well within present health guidelines.

#### 10.2 METHANOL AREA SAMPLING

Two consecutive 4-hour area samples were taken in five locations in the production area. A third sample was taken at each location on a second day. Sample times ranged from 155 to 250 minutes for individual samples and from 388 to 469 minutes for the consecutive samples. Analytical results for these samples are presented in Table 4, Section 9.

The production area samples ranged from below detectable limits (<1.0 ppm) to greater than 62.8 ppm. Even doubling the 62.8 ppm to allow for breakthrough would indicate that this area does not exceed the OSHA PEL of 200 ppm TWA. Eleven of the 13 samples analyzed have breakthrough into the back section of the sample tubes of greater than 25% of that found on the front section of the tube. As a result, those concentrations should be considered

minimum concentrations. Two samples were voided due to extreme pump unreliability; i.e., the flow rate changed significantly, and were not analyzed. Another sample was lost on analytical desorption and could not be analyzed.

Engineering controls and natural dilution ventilation appeared to be sufficient at this plant during this study to prevent over-exposure to methanol.

### General Conclusions on Methanol Exposure

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

- All workers are probably not overexposed to methanol on a short- or long-term basis unless a very major leak occurs.
- The methanol exposure is expected to be low at this plant because it is produced there. This avoids the necessity of loading and unloading trucks or rail cars, a major source of methanol exposure for operators at most formaldehyde plants.
- Area methanol concentrations are well below OSHA PEL standards.

### 10.3 EVALUATION OF ENGINEERING CONTROLS

Table 5 in Section 9 presents the analytical results of the methanol source samples. Breakthrough occurred on three of seven samples; these sample concentrations should be considered minimum concentrations.

Table 6 presents the release rates of methanol from the single and double mechanical seals tested. The results indicate that the double mechanical seals controlled the methanol release rate very well. It should be noted, however, that the fluids being pumped by these pumps did not contain pure methanol that was pumped by the single mechanical seal pump. The concentration of methanol ranged from 5 to 20 percent of the solution. The single mechanical seal released a significantly higher amount of methanol. A small leak was apparent during sampling which influenced this result.

TABLE 6. METHANOL MASS LOADINGS RELEASED FROM ENGINEERING CONTROLS

Source	Tube number	Methanol mass, $\mu\text{g}$	Sampling time, min	Daily release rate, g/d
Distillation column product pump	17	44.72	92	$7.0 \times 10^{-4}$
double mechanical seal	21	64.77	138	$6.8 \times 10^{-4}$
Absorber lower recycle pump	18	8.27	129	$9.2 \times 10^{-5}$
double mechanical seal	23	7.91	82	$1.4 \times 10^{-4}$
Methanol supply pump	46/46A	53,740/250	129	0.60
single mechanical seal	44/44A	63,743/13,434	133	0.83
	49/49A	68,206/19,567	114	1.11

In conclusion, the double mechanical seals appear very effective against leaks. The results from this survey indicate that the double mechanical seals are as good or better than any of the other seals tested in minimizing the release of methanol.

#### 10.4 FINAL CONCLUSIONS

The Celanese Chemical Company, Inc., Bishop, Texas, MO-2 unit and related storage and shipping areas use work practices, engineering controls, personal protective equipment, and natural ventilation to ensure that workers are not exposed to concentrations of methanol that exceed the limits imposed by OSHA. Samples collected from workers indicate generally low exposure concentrations. The engineering controls used appear to be very effective for control of methanol exposure.

#### REFERENCES

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2. Beasley, R. K.; Hoffman, C. E.; Rueppel, M. L., and Worley, J. W. Sampling of Formaldehyde in Air With Coated Solid Sorbent and Determination by High Performance Liquid Chromatography. Analytical Chemistry. 52(7):89-93, June 1980.

APPENDIX A

FORMALDEHYDE AND METHANOL  
SAMPLING AND ANALYSIS METHODS

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

Ronald K. Beasley, Catherine E. Hoffmann, Melvin L. Rueppel, and Jimmy W. Worley\*

Research Department, Monsanto Agricultural Products Company, 800 North Lindbergh Boulevard, St. Louis, Missouri 63166

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 84 percent, with a relative standard deviation of 0.04.

Potential occupational exposure to formaldehyde, a major industrial chemical worldwide, has been a serious concern. The concern is based on its significant irritant effects (1-3)

and on its potential to react with hydrochloric acid to form bis(chloromethyl) ether, a known carcinogen (4). The concern has intensified recently with the announcement by the Chemical Industry Institute of Toxicology (5) that preliminary results of a long-term inhalation study indicate formaldehyde is a carcinogen in rats.

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

are reported, along with the results of validation, field testing, and comparison with the widely used chromotropic acid procedure

### EXPERIMENTAL

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

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

Certified paraformaldehyde permeation tubes were purchased from Metronics Corporation.  $\alpha$ -Polyoxymethylene ( $\alpha$ -POM) permeation tubes were prepared from  $\alpha$ -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. J. 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- $\mu$ L fixed volume loop, a Waters Model 440 UV-visible absorbance detector fitted with a 340-nm wavelength kit, and a Houston Instrument Omniscrite B-5000 recorder fitted with a Spectrum 1021A filter and amplifier. A Waters C<sub>18</sub>/Corasil guard column was used with a Supelco Supelcoil LC-8 (150  $\times$  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  $\alpha$ -POM were prepared using 40 mg  $\alpha$ -POM per cm of active tube length in 1/4-in. o.d. Teflon tubing (1-mm wall thickness). Both the  $\alpha$ -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  $\alpha$ -POM and at 79 °C for paraformaldehyde. Permeation rates were 443 ng/min/cm and 96 ng/min/cm, respectively.

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

Silica gel, 12.5 g, is placed in a 100-mL round bottom (RB) flask, followed by 12.5 mL of 6 N HCl. DMF, 40 mL, is added to a 50-mL volumetric flask containing 5.0 g 2,4-DNPH. This mixture is swirled 10-15 s, quickly diluted to the mark with additional DMF, and immediately poured through a glass wool plug in a funnel into the flask containing the silica gel and HCl. The volumetric flask and glass wool are rinsed with an additional 5 mL of DMF, which is also added to the RB flask. The mixture is allowed to stand for 30 min, with occasional swirling, before isolation by vacuum filtration. The coated silica gel may be rinsed sparingly with DMF (2-3 mL). Excessive washing will result in decreased capacity for formaldehyde. It is left on the filter paper with continued suction for 1-2 min and then transferred quickly to a 100-mL RB flask. It is dried under vacuum at 55 °C for 1 h, with brief turning every 10 min. Continuous turning, as on a rotary evaporator, was found to grind the particles too finely and result in unacceptable back pressure in subsequent air sampling. Much longer drying times, as overnight, apparently completely remove residual DMF and result in decreased collection efficiency.

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

**Preparation of Sampling Tubes.** The collection device is a glass tube 10 cm  $\times$  4 mm i.d.  $\times$  1/4 in. o.d., containing a 300-mg front section and 75-mg back-up section of the coated silica gel

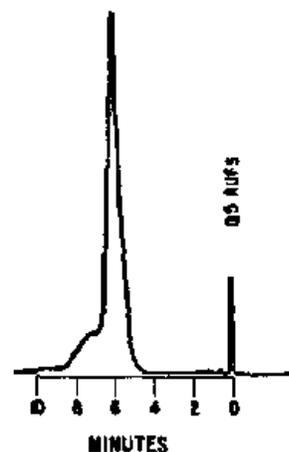


Figure 1. HPLC chromatogram for injection of 4.6  $\mu$ g of formaldehyde-2,4-dinitrophenylhydrazone (equivalent to 1.08 ppm formaldehyde in air, for a 20-L air sample).

The silica gel is retained at each end and the two sections are separated by small plugs of glass wool. It is useful to have a small indentation in the glass tube behind the back-up section to ensure the packing is held in place during sample collection.

Tubes prepared as described here were found to have a pressure drop of 7.5 in H<sub>2</sub>O at a flow rate of 115 mL/min. They have a capacity of ~123  $\mu$ g CH<sub>2</sub>O (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 (96-98% 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- $\mu$ L injection volume. The system also is flushed with CH<sub>3</sub>CN 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  $\mu$ g/mL authentic formaldehyde 2,4-dinitrophenylhydrazone in acetonitrile (corresponding to ~0.1-4.6 ppm CH<sub>2</sub>O 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

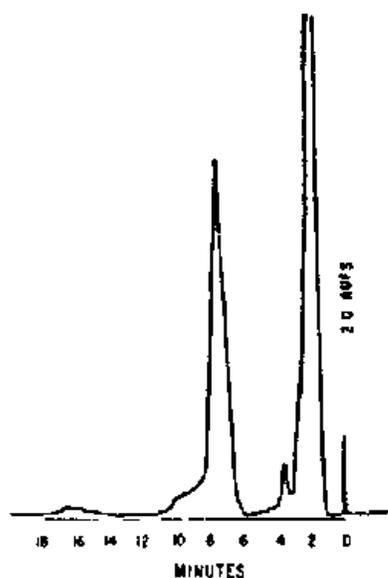


Figure 2 HPLC chromatogram for injection of sample resulting from collection of 122 µg of formaldehyde (4.96 ppm for a 20-L sample) on a 2,4-DNPH coated silica gel tube as described in the Experimental section.

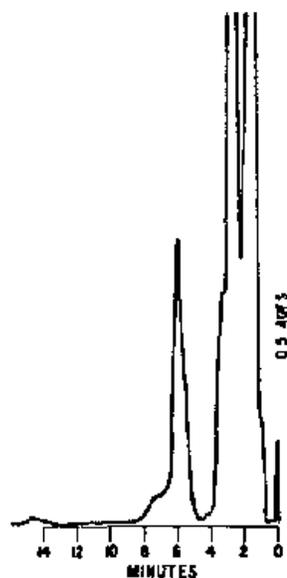


Figure 3 HPLC chromatogram for a field sample at a location where formaldehyde is used as a raw material. The sample was determined to represent 0.85 ppm formaldehyde in air.

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 (7-10) screened many solid sorbents for sampling formaldehyde and found none entirely suitable for formaldehyde retention at high humidity levels. Finally, alumina was chosen, but it could be used for only a 30-min sampling period and had to be desorbed immediately to prevent poor recovery.

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

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

Kim, Geraci, and Kupel (11) recently reported a solid sorbent procedure for formaldehyde which utilizes this concept. Formaldehyde is sampled on charcoal impregnated with an oxidizing agent, proprietary to Barney-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 Amborsorb 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  $\text{CH}_2\text{O}$  or to activate the silica gel surface. Coated solid sorbent prepared without HCl gave results 11% lower than those where HCl was used. The relative decrease was constant over a 20-fold range of formaldehyde loading, indicating it was due to decreased collection efficiency and not to decreased capacity. More striking was the effect of order of addition of reagents. Sorbent prepared in which the 2,4-DNPH was dissolved first in HCl, to preform the hydrochloride salt, followed by DMF, had a 40% decrease in collection efficiency. This result is not well understood but may have to do with wetting of the silica gel. The procedure as defined in the Experimental section has been found to reproducibly give coated silica gel with a good collection efficiency, capacity for ~5 ppm formaldehyde (for a 20-L air sample), and derivative recovery greater than 90%. However, every batch of coated silica gel should be checked in the laboratory to ensure quality before its use for field sampling.

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

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

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

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

Table I Results for Validation of Formaldehyde Method

CH <sub>2</sub> O air concn, ppm <sup>a</sup>	CH <sub>2</sub> O found, ppm <sup>b</sup>	% recovery	RSD <sup>c</sup>
0.09	0.08	89	0.0001
0.44	0.42	95	0.042
1.03	1.00	97	0.034
2.04	1.89	93	0.049
3.78	3.61	96	0.040

<sup>a</sup> Based on a 20 L air sample. Amount based on weight loss of permeation tube and time of collection at constant rate. <sup>b</sup> Average of six samples. Measurements were tested for outliers by Grubbs' test (19, 20) at the 99% confidence level. <sup>c</sup> Pooling of the individual RSDs gives the result of 0.037 with a  $\chi^2$  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  $\chi^2$  of 0.62 (critical values for  $\chi^2$  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  $\mu$ -Bondapak C<sub>18</sub> 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<sub>2</sub>O 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 0.1-3.6 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  $\mu$ g formaldehyde, obtained over a period of 3.0 h at 113 mL/min (ambient temperature, ~32 °C, relative humidity, 53%).

Some additional field results are discussed in the next section.

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

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

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

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

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

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

Table II Results of Parallel Field Tests Using 2,4-DNPH Coated Silica Gel<sup>a</sup> and Water Impingers<sup>b</sup>

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
	$\bar{X} = 2.2, \sigma = 0.3$	$\bar{X} = 1.6, \sigma = 0.2$

<sup>a</sup> Samples analyzed by the HPLC method described in the Experimental section. <sup>b</sup> 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 <sub>2</sub> O spiked, ppm	total CH <sub>2</sub> O found, ppm	ambient CH <sub>2</sub> O concn (total minus spiked)
				ppm
coated silica gel	3	0.88	1.78	0.90
coated silica gel	3	0.0	0.87	0.87
impinger	3	0.75	1.40	0.65
impinger	3	0.0	0.66	0.66

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

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

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2 1 0

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

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Analyte:	Methyl Alcohol	Method No. 559
Matrix:	Air	Range: 140-540 mg/cu m
OSHA Standard	200 ppm (260 mg/cu m)	Precision ( $CV_T$ ): 0.070
Procedure	Adsorption on silica gel, desorption with water, GC	Validation Date: 1/17/75

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### 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- $\mu$ g 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 ( $\overline{CV}_r$ ) 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 ( $\pm 5\%$ ) at the recommended flow rate. (Reference 11.3)
- 6.2 Silica gel tubes: glass tube with both ends flame sealed, 7' or long with a 6-mm O.D. and a 4-mm I.D., containing two 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- $\mu$ l, 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 Methanol Alcohol (reagent grade).
- 7.3 Purified nitrogen.
- 7.4 Prepurified hydrogen.
- 7.5 Filtered compressed air.

## E 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  $\pm 5\%$ .
  - 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<sup>®</sup>-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 1" from the first section of silica gel and broken open. The glass wool is removed and discarded. The silica gel in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of distilled water is pipetted into each sample container. Desorption should be done for 4 hours. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the water is added to minimize evaporation.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
  1. 30 ml/min (80 psig) nitrogen carrier gas flow.
  2. 30 ml/min (50 psig) hydrogen gas flow to detector.
  3. 300 ml/min (50 psig) air flow to detector.
  4. 200 C injector temperature.
  5. 300 C manifold temperature (detector).
  6. 80 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10- $\mu$ l 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  $\mu$ l 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- $\mu$ l 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  $\mu$ l to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0  $\mu$ l 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 20-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-ml 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:

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

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  $\mu\text{g}/\text{ml}$  of eluent. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in  $\mu\text{g}/\text{ml}$  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  $\mu\text{g}$ , 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.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

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 ug 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)