# HYDROGEN SULFIDE PRODUCTION IN SWINE CONFINEMENT UNITS

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#### ABSTRACT

#### HYDROGEN SULFIDE PRODUCTION IN SWINE CONFINEMENT UNITS

Ву

Gerald Leon Avery

The production of hydrogen sulfide was determined for six swine confinement buildings. The hydrogen sulfide was absorbed from air passed through a cadmium hydroxide mixture and tested for by the methylene blue method. There was a significant difference in the concentration of hydrogen sulfide between samples collected on different days at a given confinement unit, but not between samples taken on the same day at the same unit. Measurements were made in a small sample of swine finishing units of similar construction. The production of hydrogen sulfide was found to be well correlated with average outside air temperature, the ratio of the area of the pit to the volume of the building, the air retention time, and the dietary sulfur intake.

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SWINE CONFINEMENT UNITS

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Gerald Leon Avery

### A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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#### CHAPTER I

#### INTRODUCTION AND PROBLEM IDENTIFICATION

Three specific problems which stem from the practice of confinement-feeding of swine were identified by Merkel, Hazen, and Miner (1969). The first one related to odor control for the sake of the producer and his neighbors. The second one dealt with possible toxic effects of the individual gases and combinations of gases generated in the animal waste. The final problem was the potential damage to the electrical components of the confinement building.

The last two can be solved fairly easily by a good management system as they both arise from high concentrations of gas. The problem of odor control for the sake of the producer and his neighbors is more difficult to solve since the sensory threshold for a gas such as hydrogen sulfide is very low. The problem is compounded by the fact that as human population increases, so must the production of meat. Stephens (1969) noted that while the number of farms had decreased in the past, the size of each farm had increased, thus making each farm a possible site of high odor production. Also, the trend

has been for cities to grow outward toward rural areas and thus toward the meat producing areas. The large swine operation represents a very large capital investment so moving the operation to a less populated location is not a feasible alternative.

In Arizona at the end of 1971, a beef cattle feedlot which fed about 30,000 head of cattle was ordered to phase out its cattle feeding operation (Harley, 1971). In this case, the feedlot existed before a retirement community was built within two miles of the feedlot. Nevertheless, the court ruled that the feedlot was a nuisance to the retirement community.

In Clay County, Indiana, a swine farmer was charged in a suit, <u>Rice</u> vs. <u>Schopmeyer</u>, that his hogs were smelling up the community, polluting a lake in the development area and that the farmer should be enjoined from raising hogs on his farm. In this case, the judge pointed out that locality was important and what is a nuisance in one place may not be a nuisance at all in another place. The judge ruled in favor of the farmer and the farmer was allowed to continue his swine operation even though the judge recognized that "the hogs did smell a bit" (Brazil Gazette, 1973).

Matlick (1971) reported the case of a swine farmer in Michigan who was taken to court because he had constructed and operated a hog barn in such a manner as

to create offensive odors and toxic gases near his neighbor's residences. The court ruled that the farmer could continue operating his business as long as he used all the odor reduction practices that are technically feasible.

The first step in odor control is to determine the odor production rate. Merkel, Hazen, and Miner (1969) assessed swine odors as complex mixtures of amines (whose odor resembles that of ammonia) and sulfur-containing compounds which may be characterized as hydrogen sulfide. Taiganides and White (1969) determined that hydrogen sulfide was produced from the putrefaction of pig manure and found the minimum identifiable odor to be 0.7 parts per million. Since hydrogen sulfide had been identified as a primary component of the swine odor by Merkel, Hazen, and Miner (1969) and Taiganides and White (1969), and since the minimum identifiable odor was so low, and hydrogen sulfide was easy to measure in contrast to amines, volatile acids, and mercaptions, hydrogen sulfide was selected by the author as the gas that characterized the odor of swine confinement units. The object of this study was to determine the rate of production of hydrogen sulfide from some typical swine confinement buildings.

## CHAPTER II

#### OBJECTIVES

This study investigated the relationship between hydrogen sulfide generation and management practices of swine confinement units at the urban-rural interface. The specific objectives of this study were:

- To develop and assemble instrumentation for representative air sampling.
- To develop a procedure to analyze the hydrogen sulfide content of the air sample at sub-odor levels.
- 3. To measure the effect of the following parameters on the production of hydrogen sulfide:
  - a. Daily temperature.
  - b. Sulfur intake.
  - c. Air retention time.
  - d. Ratio of liquid manure area to the volume of the building.

#### CHAPTER III

## LITERATURE REVIEW

The literature review is divided into four sections. The first section discusses the general properties of hydrogen sulfide; the second section treats the factors that affect the production rates of hydrogen sulfide; the third deals with gas chromatographic methods of analysis of hydrogen sulfide; and the last section details certain chemical methods of determining the presence of hydrogen sulfide in air.

## General Properties of Hydrogen Sulfide

Hydrogen sulfide is a colorless gas and has a pungent odor characteristic of rotten eggs. The relative density of hydrogen sulfide to air is 1.19. Scott (1939) discovered hydrogen sulfide to be a noncumulative poison which is rapidly oxidized by the blood into nontoxic products. Concentrations of hydrogen sulfide in the air of 0.01 percent to 0.015 percent may produce death in 8 to 48 hours if breathed continuously. In higher concentrations the action of the hydrogen sulfide is so

rapid that the only symptoms of acute poisoning are sudden nausea and unconsciousness, followed by death. Jennings (1957) and Taiganides and White (1969) found that the maximum average atmospheric concentration of hydrogen sulfide to which workers may be exposed for an eight hour working day without injury to health is 20 parts per million.

In the agricultural air pollution field the level of odor threshold concentration is of importance because this is the level where human welfare is jeopardized. Wilby (1969) indicated the odor threshold concentration of hydrogen sulfide to be 0.0045 parts per million. Taiganides and White (1969) reported the odor threshold level to be 0.7 parts per million. Odor should not be relied upon to give adequate warning because the human sense of smell can be fatigued rapidly, so that high concentrations of hydrogen sulfide do not give a proportional high sense of odor.

The solubility of a gas was reported by Merkel, Hazen, and Miner (1969) to be very important in determining the odor levels. If the solubility of a gas was very low it would escape from the manure as soon as it was produced and produce very high odor levels if the production rate was very high. The situation was different for gases which were very soluble in water because even if the production rate of these gases were

high it would have little effect on odor levels since the gases would not escape to the air. The reason why the concentration of hydrogen sulfide in swine confinement units does not normally reach levels which are dangerous to the pigs is because hydrogen sulfide is soluble in water. Since hydrogen sulfide is soluble in water the concentrations of hydrogen sulfide in swine units are low and therefore very hard to determine.

There exists a great need to determine an odor intensity classification because such information has been used in lawsuits as evidence of a nuisance. Fichte (1971) and Harley (1971) reported on a lawsuit against an Arizona beef cattle feedlot where a witness kept an odor diary. In this diary the witness had recorded feedlot odors by time and intensity. The intensity of the odors was based on a subjective olfactory test where the intensity ranged from slightly noticeable, which was rated one, to intolerable, which was rated five. Matlick (1971) reported on a lawsuit against a Michigan swine farmer where a witness testified that an odor problem existed 63 days in a 7 month period. Eleven of the 63 days were classified bad, with 7 more classified as being very bad.

Barth and Polkowski (1971) identified the source of hydrogen sulfide in swine housing units to be the decomposition of manure. The proteins decompose to

ammonia, volatile organic acids, mercaptans, and hydrogen sulfide. Merkel, Hazen, and Miner (1969) found protein in manure to contain on the average 1 percent sulfur. Taiganides and Hazen (1966) found that 1,000 gallons of fresh hog manure contained 12 pounds of sulfur.

## Factors Affecting Production of Hydrogen Sulfide

Ludington, Sobel, and Hashimoto (1969) stored chicken manure in a diluted state and in an undiluted state. In this experiment all the other factors were kept constant and the diluted manure produced significantly more hydrogen sulfide. This is a serious problem with today's animal confinement units where the waste is handled in a liquid form, water being added to make a slurry.

White (1969) increased the temperature of stored dairy manure and discovered an increase in odor production due to hydrogen sulfide. The reasons given for increased odor were an increase in vaporization with higher temperatures and an increase in the biological reactions which follow the van't Hoff rule of reaction rate doubling for each 10 degrees Centigrade increase in temperature over a restricted temperature range which includes the ambient temperatures. White (1969) also discovered that the end products of anaerobic decomposition of animal wastes contained hydrogen sulfide but under aerobic conditions no hydrogen sulfide was produced.

Merkel, Hazen, and Miner (1969) and Sawyer (1960) found the solubility of hydrogen sulfide and hence the odor of a solution is markedly influenced by the solution's pH. At pH values of eight and above, most of the reduced sulfur exists in solution as HS<sup>-</sup> and S<sup>=</sup> ions and the amount of hydrogen sulfide is negligible. At pH levels below eight, the equilibrium shifts rapidly towards the formation of un-ionized hydrogen sulfide and is about 80 percent complete at pH seven. Therefore at pH values of seven or lower, the partial pressure of hydrogen sulfide becomes great enough to cause serious odor problems.

## Gas Chromatographic Methods of Analysis for Hydrogen Sulfide in Air

Kappe and Adams (1967) tried to inject ambient air samples into a gas chromatograph and detect the sulfur compounds present. It was determined that the detection of sulfur compounds was only possible after a 10- to 50-fold concentration of the sample.

Burnett (1969) analyzed a sample of liquid manure volatiles obtained by the precolumn trapping technique. A chromatogram was obtained which had 14 peaks. The gas from one of the peaks corresponded to an odor of rotten eggs and was tentatively identified as hydrogen sulfide.

An odor confirmation test was then performed and the odor tentatively identified as hydrogen sulfide was confirmed to smell like the authentic compound.

Merkel, Hazen, and Miner (1969) found that the gas chromatograph could be used in identification of the gases present in the atmosphere of the swine confinement unit if the samples were first concentrated by the regeneration technique. The presence of alcohols, amines, amides, mercaptans, sulfides, disulfides, ammonia, and organic intermediates were determined. Merkel, Hazen, and Miner (1969) did not, however, successfully determine the concentrations of these gases.

White and Taiganides (1969) used the equilibration sampling method to concentrate the samples. In equilibration sampling, organic volatiles are passed over a liquid stationary phase until the whole amount of the stationary phase reaches full equilibrium with the organic volatiles. Using a non-polar stationary phase permits trapping the oragnic compounds while most of the water vapor passes through. Flame ionization detectors were used for this work. A chromatogram from this experiment indicated that some 40 to 50 different compounds were present in the head space gas over dairy cattle waste. White (1969) used this same technique and was able to identify one of the peaks as being hydrogen sulfide. He also measured peak height and the intensity

of the odors passing through the gas chromatograph as a function of pH, aeration, and electrode potential.

## <u>Chemical Methods for Determining</u> <u>the Presence of Hydrogen</u> Sulfide in Air

Chemical oxygen demand (COD) analysis was used by Trus, Hazen, and Miner (1969) to quantify odors in a swine building. The COD test measures the total quantity of oxygen required for oxidation of organic compounds to It is based upon the fact that carbon dioxide and water. most organic compounds can be oxidized by a strong oxidizing agent under acid conditions. Acidified potassium dichromate is used as the oxidizing agent. The COD technique is sensitive to the rate of dilution by ventilation air. There was no correlation between air COD values and the manure temperature or manure COD. The COD method was shown to have good correlation in measuring hydrogen sulfide. It was not determined whether air COD was an overall measure of the level of organic gases or whether one gas or a combination of gases was predominant.

Pare (1966) tested and determined that the lead acetate paper tape reagent method for the estimation of hydrogen sulfide in air was not acceptable as a stoichiometric reagent in any case where long duration sampling periods are concerned. A new mercuric chloride paper tape

reagent has been developed as a substitute and was an adequate analytical tool for the estimation of hydrogen sulfide in air as long as the concentration were less than 60 parts per billion. Day, Hansen, and Anderson (1965) also used the lead acetate paper to detect the presence--but not the concentration--of hydrogen sulfide.

Other metallic compounds are potential indicators of the presence of hydrogen sulfide. Some of the effects showing the presence of hydrogen sulfide were black accumulations formed on copper thermostat elements and white accumulations on galvanized tanks (Day, Hansen, and Anderson, 1965).

Stephens (1971) investigated paper chromatography as a method of odor identification. In this method, a piece of filter paper was spotted near one corner with the sample to be analyzed. A solvent is then allowed to move along the paper by capillary action. This moves the components of the mixture along the paper until they are separated. The separated spots must then be detected with a suitable chemical reagent.

Barth and Polkowski (1971) used a selective gas absorption chain to determine the hydrogen sulfide concentration in air. The test was conducted for a period of 15 hours during which time about ten cubic feet of air passed through the absorption tubes. Tubes one and two contained boric acid indicator solution used in

supernatant ammonia determination. The third tube in the series contained zinc acetate solution plus distilled water for collecting hydrogen sulfide. Iodine solution was added to tube three to react with the sulfide. Then hydrochloric acid was added and the solution was thoroughly mixed. The mixture was back-titrated with sodium thiosulfate using starch as an indicator.

Fogo and Popowski (1949) absorbed hydrogen sulfide from a stream of gas in a suspension formed by adding sodium hydroxide to a solution of zinc acetate. The suspension containing the absorbed sulfide as zinc sulfide was then treated with an acid solution of p-aminodimethylaniline, followed by the addition of a small amount of ferric chloride solution. After time was allowed for the formation of methylene blue, the solution was diluted in a volumetric flask and an aliquot was transferred to the spectrophotometer for measurement. This method is very sensitive to temperature and must be conducted at between 20°C and 30°C. This method was sensitive to about three and one-half micrograms and the amount of sample to be taken should be that which would contain between 35 and 350 micrograms.

Jacobs (1960) used the cadmium sulfide method of determining the concentration of hydrogen sulfide in air. This method was based on the precipitation of cadmium sulfide in weakly acidic solution of a cadmium salt. The

amount of cadmium sulfide precipitate was then estimated iodometrically. This method was accurate to about onehalf part per million for a 30 liter air sample when testing air whose concentration of hydrogen sulfide was within the range of hygienic significance. This was considered the method of choice in industrial work where detection of relatively high concentration levels of 10 parts per million and above were desired.

Jacobs, Braverman, and Hochheiser (1957) devised the methylene blue method of analyzing the concentration of hydrogen sulfide in air. In this method air was bubbled through a mixture of an alkaline suspension of cadmium hydroxide at a rate from one tenth of a cubic foot per minute to one cubic foot per minute for a period of 15 minutes. The concentration of the trapped sulfides was then estimated by the methylene blue method. The principle of this method is that the sulfide ion reacts with p-aminodimethyltaniline and ferric chloride to yield methylene blue which is determined spectrophotometrically or colormetrically. With this method, the hydrogen sulfide concentration can be determined in the parts-per-billion range. Katz (1969) calculated the sensitivity of this method to be 0.01 part per million for a 30 liter air sample whose concentration was between 0.05 part per million and 10.0 parts per million of hydrogen sulfide.

Budd and Bewick (1952) determined that the formation of methylene blue proceeded according to the following reactions. First the N, N-dimethyl-p-phenylenediamine was oxidized by the ferric chloride. The resulting compound then oxidized the hydrogen sulfide to methylene blue sulfate which was the compound measured colorimetrically. This process is presented symbolically in Figure 1.







Figure 1.--Formation of methylene blue.

#### CHAPTER IV

#### EXPERIMENTAL PROCEDURE

This section was organized such that the following subsections appear in the order that this project was conducted.

## Air Sampling Machine

The air sampling machine was built to take eight air samples in a 24-hour period. The machine was equipped with a 24-hour clock which could be set at 15 minute intervals. The clock controlled a stepping switch which advanced one position each time the signal from the clock to the switch was interrupted. Eight normallyclosed solenoid valves were controlled by the stepping switch so that only one valve at a time would open to take an air sample. The duration of sampling was controlled by the time clock. One normally-open solenoid valve was also controlled by the stepping switch so that it would close when one of the sample solenoid valves opened. This valve permitted the suction pump to run continuously pulling air constantly through the machine. Thus when a sample solenoid valve opened fresh air from the source would be immediately sampled. Each

solenoid valve had a midget impinger attached to it on the fresh air side. Two different types of midget impinger are shown in Figure 3. The midget impinger contained an absorption mixture through which the air sample was bubbled. A manifold was located on the pump side of the solenoid valves and on the fresh air side of the impingers. The manifolds kept fresh air at each impinger and made it necessary to have only one tube running from the fresh air manifold to the air sampling source. The tubing used was Tygon flexible plastic tubing with a diameter of 0.953 cm.

Between the pump and the pump manifold a gas flow meter and a screw clamp were installed to measure and control the air flow rate. A switch was used to turn the pump off after the eighth sample was collected to prevent recycling of the air sampling sequence. Figure 2 is a diagram showing the air flow when the device was in a non-sampling mode. During sampling, the air flowed through an impinger and a normally-closed solenoid valve instead of the normally-open solenoid. Figure 4 is a top view of the air sampling machine with the cover open. Figure 5 is a front view of the air sampling machine with the front panel removed.



Sampling Source

Figure 2.--Air flow diagram for the air sampling machine when not taking an air sample.



Figure 3.--Two types of midget impingers.



Figure 4.--Top view of air sampling machine.



Figure 5.--Front view of air sampling machine.



Figure 6.--The air sampling machine in a swine building.

## Standardizing Hydrogen Sulfide Stock Solution

A standard potassium dichromate solution and a starch solution were prepared; these two solutions were used to standardize the standard sodium thiosulfate titrant. The standard sodium thiosulfate titrant and the starch solution were then needed to prepare the iodine solution. The preparation of the hydrogen sulfide solution required addition of the iodine solution which was then titrated with the standard sodium thiosulfate solution. The starch solution was used as the indicator for the endpoint of titration. The recipes for these solutions are given in Appendix A.

## Sample Testing Solutions

The cadmium hydroxide absorption mixture was used to trap the hydrogen sulfide. The ferric chloride solution and the amine-sulfuric acid test solution were then added to the trapped hydrogen sulfide to form methylene blue. The procedures used to prepare these solutions are presented in the following subsections.

## Cadmium Hydroxide Absorption Mixture

The cadmium hydroxide absorption mixture was prepared as follows:

a. 4.3 g of 3  $CdSO_4 \cdot 8H_2O$  was dissolved in 475 ml of distilled water.

- b. 0.3 g of sodium hydroxide was dissolved in
  475 ml of distilled water.
- c. The sodium hydroxide solution was slowly added to the cadmium sulfate solution with constant mixing.
- d. The solution of part (c) was diluted to one liter with distilled water. This solution must be mixed well before using.

## Ferric Chloride Solution

The ferric chloride solution was prepared by dissolving 100 g of ferric chloride hexahydrate in 80 ml of distilled water. This solution was diluted to 100 ml with distilled water.

## Amine-sulfuric Acid Stock Solution

The preparation of the amine-sulfuric acid stock solution was accomplished as follows:

- a. 50 ml of concentrated sulfuric acid was added to 30 ml of distilled water and cooled to room temperature.
- b. 12 g of N,N-dimethyl-p-phenylenediamine was added to the solution of part (a) and the mixture was stirred until the solution was homogeneous.

## Amine-sulfuric Acid Test Solution

The amine-sulfuric acid test solution was prepared by diluting 25 ml of the amine-sulfuric acid stock solution to one liter with a 1-1 sulfuric acid solution. The 1-1 sulfuric acid solution was prepared by adding 500 ml of sulfuric acid to 500 ml of distilled water.

## Preparation of Standard Curves

The following procedure was used to obtain the data for the standard curves.

- a. 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90,
  100, 120, 140, 160, 180, and 200 μg of
  hydrogen sulfide (in an aqueous solution) was
  added separately to 50 ml volumetric flasks
  which contained 45 ml of the cadmium hydroxide
  absorption mixture. Each flask was then stirred.
- b. 0.6 ml of the amine test solution was added to each flask which was then stirred.
- c. One drop of the ferric chloride solution was similarly added to each flask which was stirred and diluted to 50 ml with distilled water.
- d. The first mixture containing no hydrogen sulfide was transferred to the colorimeter cell of the Fisher AC Model Colorimeter which contained a 650 µm red filter.

e. The colorimeter was adjusted to zero with the blank and then the transmittances of the 16 remaining samples were read and recorded.

## Test of 30 Minute Waiting Period

Jacobs, Braverman, and Hochheiser (1957) recommended a wait of 30 minutes before placing the samples into the colorimeter cell. The following test was conducted to see if this waiting period was necessary. Samples of 20 and 100  $\mu$ g of hydrogen sulfide were tested with and without the thirty minute waiting period.

#### Sample Testing

The procedure that was used to test each air sample was as follows.

- a. 10 ml of the cadmium hydroxide was added to a midget impinger and air was bubbled through the mixture at a rate of 2.83 liters per minute for the desired time.
- b. 0.6 ml of the amine test solution was added to a blank and to each sample. These samples were then agitated.
- c. One drop of the ferric chloride solution was similarly added to each sample and the blank.
- d. The blank and each sample were diluted with distilled water to 50 ml in 50 ml volumetric flasks.

e. The colorimeter cell was set to zero with the blank and the transmittance of each of the samples was read and recorded.

#### Sampling Procedure

The air sampling machine was placed within the swine building (see Figure 6) and the sample was taken inside the building at a distance of 0.3 m behind the exhaust fan at a height of 1.2 m. The duration of the sampling time for each sample was 14 minutes if the sample concentration was expected to be over 1.5 ppm. (The time was actually 14 minutes when the time clock was set for 15 minutes.) If the concentration of the sample was expected to be under 1.5 ppm, the sampling time for each sample was 30 minutes. The first sample was taken at 9:00 a.m. and the other seven samples were taken at three hour intervals after the first sample. Ten days' collection of samples were taken from each building over a period of two to three weeks.

## Quantity of Exhaust Air

The exhaust flow for each fan was determined by the following procedure. First the area of each fan was divided into six equal areas as shown in Figure 7. The first area was delineated by a circle in the middle of the fan area and each of the other five areas was bounded by a concentric ring around the first area. The velocity



(Velocity readings were taken at the X's) Figure 7.--The six equal areas of the fan.
of the air flow was measured along a radius of the fan at the midpoint of the radial distance between the boundaries of each equal area. The measurement was made inside the building at a distance of 4 cm from the fan with a Alnor Thermo-Anemometer, type 8500, which had an accuracy of plus or minus 3 percent of the indicated value. The six velocity readings were averaged and multiplied by the fan area to obtain the air flow rate.

Some of the buildings sampled had a second fan that would cycle on and off depending on air temperatures within the building. The on-off fans were wired with an event recorder to determine the total time they were operating so that total air flow could be determined.

#### CHAPTER V

#### RESULTS OF EXPERIMENTAL INVESTIGATIONS

# Description of Swine Units

Unit no. 1 was a farrowing house with aluminum siding which had a partial pit running down the center of the building. The unique feature of unit no. 1 was that Wham, a commercial product, was used to control odor production. Wham was a dichlorobenzene coupound made by the Hercules Chemical Company. Wham is designed to reduce odors by reducing the bacterial decomposition of the manure. Figure 8 is a diagram showing the floor plan of unit no. 1.

Unit no. 2 (see Figure 9) was a farrowing house that was converted from a poultry housing unit. It was a wooden building which had an aluminum roof. The unique feature of unit no. 2 was the pit which was constructed on top of the former floor and was built only under the farrowing crates. There was a covered trough connecting the three lengths of pit which allowed the pits to be pumped from one location.

Units no. 3, 4, 5, and 6 (see Figures 10, 11, 12, and 13 respectively) were finishing buildings with







Building Height = 2.13m Pit Depth = 0.6lm Pit Length = 27.43m Pit Width = 2.44m

Figure 9.--Unit no. 2 floor plan.



Building Height = 2.06m Pit Depth = 0.61m

Figure 10.--Unit no. 3 floor plan.



Figure 11.--Unit no. 4 floor plan.



Building Height = 2.44m Pit Depth 1.22m

Figure 12.--Unit no. 5 floor plan.



Building Height 2.44m Pit Depth = 1.68m

Figure 13.--Unit no. 6 floor plan.

aluminum roofs and siding. Units no. 3 and 4 had pits which were under the entire floor. Units no. 5 and 6 had partial pits which were located along the outer walls and along a center line, respectively, of the building. Another unique feature of units no. 5 and 6 was that the pigs were fed high moisture corn instead of ground dry corn.

Units no. 4 and 5 each had two continuous fans and the other four units were equipped with one continuous far and one on-off fan.

The weights of the pigs in each unit were based on the farmers' estimate of their actual weight. Table 1 contains the number of hogs, the average weight of the hogs, and the ventilation data for each of the six swine units tested.

# Results of 30 Minute Waiting Period Tests

The concentration of the  $20 \ \mu$ g sample without the 30 minute waiting period was 0.50 ppm and it was also 0.50 ppm with the 30 minute waiting period. The concentration of the 100  $\mu$ g sample was determined to be 2.99 ppm with and without the 30 minute waiting period.

#### Standard Curves

The concentration of hydrogen sulfide in ppm was equal to the mass in micrograms of dissolved hydrogen

		rime ( <u>day</u> )	140	216	833	1440	1440	418
	On Off Fan	Vel. ( <u>m</u> )	317.50	396.24	327.66	245.11	130.81	161.18
•		Dia.(m)	0.61	0.56	16.0	0.61	0.61	0.61
Six Units	ous Fan	Vel. ( <u>m</u> )	181.86	406.40	396.24	228.09	136.14	161.18
for the	Continuc	Dia.(m)	0.61	0.41	0.56	0.61	0.61	0.61
ilation Data	Ave. Mass	Wt. (kg)	158.78 4.54	158.78 4.54	32.02	40.82	68.04	58.97
and Vent	No. of	Pigs	153	408	450	720	450	262
1Swine	No. of	Sows	18	48				
TABLE	Unit	.ov	н	2	m	4	ß	9

sulfide added to the sample multiplied by 0.719 divided by the volume in liters of the air sample (Jacobs, Braverman, and Hochheiser, 1957). The results of the preparation of the standard curves are presented in Table 2. Figure 14 gives the standard curve for the 14 minute sampling period and Figure 15 gives the standard curve for the 30 minute sampling time.

# Efficiency of Hydrogen Sulfide Trapping

The trapping efficiency of hydrogen sulfide was tested by connecting three midget impingers in series so that the air sample was drawn through all three impingers. The results when the air samples contained 0.11 ppm and 1.05 ppm of hydrogen sulfide were 100.0 percent recovery by the first impinger for both concentrations. When the air contained 3.12 ppm of hydrogen sulfide the results were 99.4 percent recovery by the first impinger and 100.0 percent recovery by the first impingers. Table 3 gives the results of the efficiency of the trapping of hydrogen sulfide.

#### Sample Data

The sample concentration data, the time the onoff fan was operating, and the daily average temperatures for each unit tested are presented in Appendix B. The average temperature was obtained by averaging the daily

µg of hydrogen sulfide	percent transmittance	ppm for the 30 minute sample	ppm for the 14 minute sample
0	100.0	0.00	0.00
5	96.5	0.04	0.10
10	93.7	0.08	0.18
20	91.7	0.17	0.36
30	87.0	0.25	0.54
40	85.5	0.34	0.72
50	81.0	0.42	0.91
60	79.0	0.51	1.09
70	77.0	0.59	1.27
80	72.6	0.68	1.45
90	70.5	0.76	1.63
100	68.5	0.85	1.81
120	65.6	1.02	2.18
140	62.5	1.18	2.54
160	60.0	1.36	2.90
180	57.0	1.52	3.26
200	54.0	1.69	3.63

TABLE 2.--Data for Standard Curves.

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Figure 14.--Standard curve for the 14 minute samples.



Figure 15.--Standard curve for the 30 minute samples.

Concentration of Hydrogen Sulfide in ppm	Percent Hydrogen Sulfide Trapped
0.11	100.0
1.05	100.0
3.12	99.4

TAELE 3.--Efficiency of Hydrogen Sulfide Trapping.

maximum temperature and the daily minimum temperature from data taken at the Agricultural Experiment Station Horiculture Farm which was located at East Lansing, Michigan. The average temperature for the 10 day period for each unit is presented in Table 4.

Unit no. 1 had Wham (a product manufactured by Hercules Chemical Company to reduce odors) added to the pit every 14 days. It was added on September 16, 1972, while sampling was being conducted.

The testing time for each sample for unit no. 2 was 14 minutes while the sampling time for the five remaining units was 30 minutes each.

The average concentration of the 80 samples for each unit are presented in Table 4.

#### Sulfur Intake

The nursing pigs at units no. 1 and 2 were fed commercial pellets for nursing pigs. The pigs at units no. 5 and 6 were fed high moisture corn and a commercial soybean supplement. The rest of the pigs at the other units consumed a ground corn and soybean mixture.

The amount of feed consumed by the pigs was based on the farmer's estimate of the amount of feed that was fed to the pigs in each unit. The percent protein and the percent sulfur that the feed contained were based on the values given by Morrison (1951) and an animal TABLE 4.--Values of Parameters for Correlation Analysis.

Parameter	Unit 1	Unit 2	Unit 3	Unit 4	Unit 5	Unit 6
Average Hydrogen Sulfide Production in g per 100 kg -2 of Pig Mass Weight times 10	0.047	0.295	0.113	0.086	0.007	0.010
Average Concentration of Hydrogen Sulfide in ppm	0.123	2.174	0.358	0.847	0.126	0.120
Average Air Temperature for the Ten Day Sampling Period in <sup>O</sup> C.	16.7	5.5	3.2	-2.5	-4.0	-2.4
Ratio of Area of Pit per Volume of Building in m <sup>-l</sup>	0.252	0.267	0.485	0.424	0.126	0.173
Air Retention Time in Minutes	5.31	10.71	1.72	5.54	9.31	8.27
Daily Sulfur Intake in g per 100 kg of Pig Mass Weight	9.821	9.758	24.000	21.000	7.500	10.000

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nutritionist (Miller, 1973). The daily feed consumed by the pigs as a percent of their body mass, the protein content of the feed, and the sulfur content of the feed are presented in Table 5. The total sulfur consumed daily by the pigs was calculated and presented in Table 4 as grams of sulfur per 100 kg of pig body mass.

#### Retention Time

The retention time for air within each building was calculated as the volume of the unit divided by the average daily air flow through the building. The retention time is presented in Table 4.

## Ratio of Area of Pit to Volume of Building

Each building was measured and the area of the pit and volume of the building were calculated. The ratio of the area of the pit to building volume was then determined and is presented in Table 4.

#### Production of Hydrogen Sulfide

The daily production of hydrogen sulfide was calculated as the average daily concentration of hydrogen sulfide multiplied by the total daily air flow. The average daily production of hydrogen sulfide was determined by averaging the 10 daily production rates of hydrogen sulfide. The average daily production of hydrogen

ant Sulfur Conten of Feed (percent)	0.33 0.33	0.30 0.33	0.30	0.30	0.25	0.25
Protein Conte of Feed (percent)	16.0 18.0	16.0 18.0	16.0	16.0	13.0	13.0
Daily Feed Consumption (percent of Ave. Mass Wt.)	3.0 4.0	3.0 4.0	8.0	7.0	3.0	4 • 0
Average Mass Weight of Pigs (kg)	158.78 4.54	158.78 4.54	32.02	40.82	68.04	58.97
Unit No.	ы	2	ſ	4	വ	9

TABLE 5.--Feed and Sulfur Intake Data.

sulfide for the 10 sampling days for each of the six units in grams per 100 kg of pig body mass is presented in Table 4.

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#### CHAPTER VI

#### DISCUSSION OF RESULTS

# Variation of Hourly and Daily Data

The results of a two-way analysis of variance on the data obtained from each unit are presented in Table 6. Table 6 shows that there were no significant differences between the samples taken at different hours but that there were highly significant differences between samples taken on different days of the sampling period. The difference between days is thought to have been due to the large average temperature differences between days which was as high as 12.4 degrees Centigrade.

#### Tests of Sampling Procedure

In Chapter V, p. 33, it was determined that there was no difference in the sample results if the 30 minute color-development period was omitted. Therefore there was no 30 minute waiting period when the standard curves were prepared and when the air samples were tested.

The recovery of the hydrogen sulfide varied from 100.0 percent at 0.11 ppm and 1.05 ppm to 99.4 percent at 3.12 ppm. This recovery rate was so high that the

Source		df	SS	EMS	F(1)
Unit No.	1				
Day Hour Error		9 7 63	0.0522 0.0093 0.0953	0.0058 0.0013 0.0015	3.86** 0.86ns
Unit No.	2				
Day Hour Error		9 7 63	49.2251 1.0924 8.5962	5.4694 0.1560 0.1364	40.10** 1.14ns
Unit No.	3				
Day Hour Error		9 7 63	0.1529 0.0210 0.1770	0.0170 0.0030 0.0028	6.07** 1.07ns
Unit No.	4				
Day Hour Error		9 7 63	3.1091 0.4893 2.4267	0.3454 0.0699 0.0385	8.97** 1.8lns
Unit No.	5				
Day Hour Error		9 7 63	0.0149 0.0049 0.0216	0.0016 0.0017 0.0003	5.33** 2.23ns
Unit No.	6				
Day Hour Error		9 7 63	0.0155 0.0010 0.0108	0.0017 0.0001 0.0002	8.50** 0.50ns

TABLE 6.--Two-Way Analysis of Variance of the Air Sampling Data.

(1)\*\* means significant at the 0.01 level and ns means not significant at the 0.05 level.

data obtained from this method were assumed to represent the true situation.

# Factors That Affect Hydrogen Sulfide Production

The correlation of average hydrogen sulfide production to average air temperature of the sampling period for unit nos. 3, 4, 5, and 6 was 0.7876. The correlation decreased sharply to 0.1890 when unit no. 1 was included. When all six units were considered the correlation coefficient increased to 0.2321. This evidence indicates that Wham (a product manufactured by Hercules Chemical Company to reduce odors) was effective at least at the higher temperatures encountered while sampling unit no. 1.

The correlation of average hydrogen sulfide production with the ratio of the area of the pit per volume of the building for unit nos. 3, 4, 5, and 6 was 0.9949. The correlation coefficient decreased only slightly to 0.9919 when unit no. 1 was included. When all six units were considered the correlation coefficient dropped to 0.3164. Unit no. 2 had its pit constructed on top of the former chicken coop floor. This type of construction exposed the sides of the pit to the temperatures of the air inside the building. It is felt that this caused the unexpected increase in the production of hydrogen sulfide in unit no. 2. The correlation of average hydrogen sulfide production to the air retention time for unit nos. 3, 4, 5, and 6 was -0.9557 and was -0.9359 when unit no. 1 was included. When all six units were considered the correlation coefficient was 0.2439. Unit no. 2 had the highest hydrogen sulfide production rate and during the last seven days of sampling the motor on the on-off fan burned out which also gave unit no. 2 the longest retention time and caused the poor correlation coefficient.

The correlation of average hydrogen sulfide production to the amount of sulfur intake was 0.9937 for unit nos. 3, 4, 5, and 6 and decreased slightly to 0.9526 when unit no. 1 was included. When all six units were considered the correlation coefficient dropped to 0.1013. The unusual type of pit construction in unit no. 2 probably caused this poor correlation by increasing the production of hydrogen sulfide.

#### CHAPTER VII

#### SUMMARY

Hydrogen sulfide was trapped by a cadmium hydroxide solution and tested colorimetrically by the methylene blue method which was determined to be a very effective technique.

The length of the sampling period was 10 days at each building and eight samples were taken each day from the two swine farrowing units and four swine finishing units. The concentration of hydrogen sulfide of each sample was determined as well as the quantity of exhaust air, the number and weight of the pigs present in the building, the average outside air temperature, and the sulfur intake for each of the six swine units.

There was a significant difference in the concentration of hydrogen sulfide between samples taken on different days. There was no significant difference in the concentration of hydrogen sulfide between samples taken at different times of the same day.

For buildings of similar construction the production rate of hydrogen sulfide was closely correlated

to the average outside air temperature, the ratio of the area of the pit per volume of the building, the building air retention time, and the sulfur intake.

#### CHAPTER VIII

#### CONCLUSIONS

 The cadmium hydroxide-methylene blue method was a very effective procedure for trapping and testing for hydrogen sulfide in swine confinement units.

2. There was no significant difference at the five percent level of hydrogen sulfide content between samples taken at different times of the day.

3. There was a significant difference at the one percent level of the hydrogen sulfide content between samples taken on different days.

4. The production of hydrogen sulfide was highly correlated with the following parameters for swine finishing buildings of similar construction:

- a. the average outside air temperature
- b. the ratio of the area of the pit per volume of the building
- c. the air retention time for the building
- d. the daily sulfur intake.

However, it must be stated that the sample size was small (6) and some data were rejected (2) where anomalies could be rationally explained.

#### CHAPTER IX

#### SUGGESTIONS FOR FUTURE WORK

It would be very desirable if several samples could be taken over a long period of time on one swine unit to determine if there is a yearly trend in the production of hydrogen sulfide. If this is done, the author believes that one very important parameter to measure, in addition to the ones measured in this project, is the temperature of the manure in the pit.

It would be very beneficial to conduct a controlled experiment in which the pit is treated with Wham (a chemical product manufactured by the Hercules Chemical Company to reduce odors) to determine its effect on the reduction of hydrogen sulfide production.

The testing procedure developed in this thesis should be used to measure the hydrogen sulfide concentration outside the swine building. Such data could benefit both the farmer in planning the location of new swine buildings and the developer in planning the location of new homes in the vicinity of a swine building.

The author learned to estimate the concentration of hydrogen sulfide inside the swine units even though

some of the concentrations were below the odor threshhold. The author's sense of smell was the basis of the estimates. Since the author felt that the hydrogen sulfide concentration was correlated to the apparent odor level, hydrogen sulfide could be used as a tracer gas for tracing odor transmission from a swine building. REFERENCES

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APPENDICES

#### APPENDIX A

# SOLUTIONS FOR STANDARDIZING HYDROGEN SULFIDE STOCK SOLUTION

## Standard Potassium Dichromate Solution

The preparation of 0.025 N standard potassium dichromate solution was done as follows:

- The potassium dichromate was dried for two hours at 103°C.
- b. 1.226 g of potassium dichromate was added to distilled water and diluted to one liter with distilled water.

## Starch Solution

The preparation of the starch solution was accomplished as follows:

- a. An emulsion of 5 g of soluble starch was prepared in a beaker with a small quantity of distilled water.
- b. The emulsion was poured into 1 liter of boiling distilled water, boiled for 5 minutes and allowed to settle overnight.

- c. The clear supernate was decanted and used for the starch solution.
- d. The starch solution was preserved by adding four drops of toluene.

## Standard Sodium Thiosulfate Titrant

The 0.025 N sodium thiosulfate titrant was prepared by the following steps:

- a. 6.205 g of  $Na_2S_2O_3 \cdot 5H_2O$  were dissolved in freshly boiled and cooled distilled water and diluted to one liter.
- b. 2 g of potassium iodide, free from iodate,
   was similarly dissolved in an erlenmeyer
   flask with 150 ml of distilled water.
- c. 10 ml of 1 part distilled water and 9 parts sulfuric acid were then added.
- d. Exactly 20 ml of the standard dichromate solution were added next.
- e. The mixture was placed in the dark for 5 minutes, dilluted to 400 ml with distilled water, and titrated with the thiosulfate solution. Starch was added toward the end of the titration when a pale straw color was reached.
- f. The sodium thiosulfate solution should be adjusted to exactly 0.025 N.

#### Iodine Solution

The preparation of the 0.025 N iodine solution was accomplished as follows:

- a. 25 g of potassium iodide was dissolved in
  100 ml of distilled water.
- b. 3.175 g of iodine were added next and after the iodine had dissolved, the solution was diluted to 1 liter with distilled water.
- c. The resulting solution was standardized against 0.025 N sodium thiosulfate, using the starch solution as the indicator.
- d. Finally, the iodine solution was adjusted to exactly 0.025 N.

#### Hydrogen Sulfide Stock Solution

The preparation of the hydrogen sulfide stock solution was done as follows:

- a. 0.71 g of Na<sub>2</sub>S·9H<sub>2</sub>O was dissolved in 1 liter of distilled water.
- b. 15 ml of the iodine solution was added to50 ml of the sodium sulfide solution.
- c. 5 ml of concentrated hydrochloric acid was added next and the solution was agitated.
- d. The liquid was transferred to a beaker and back titrated with 0.025 N sodium thiosulfate titrant. The starch solution was used as an indicator.

e. mg/l total sulfide as  $S^{=}$  equals

(ml iodine - ml thiosulfate titrant) 400 ml sample

f. The hydrogen sulfide stock solution was adjusted so 1 ml of solution was equal to 100  $\mu$  g of hydrogen sulfide.

Tested.
Units
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for
Data
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APPENDIX

						the second s				
0+e(	Τi	me and	Conce	ntrati	on in	ppm of \$	Sample	ß	Fan Operation	Average Temp.
	9 am	Noon	3 pm	e pm	und 6	midnight	3 am	6 am	Time (min).	(c))
Unit No. 1										
9-20-72	0.09	0.08	0.08	0.16	0.17	0.12	0.13	0.11	195	17.5
9-22-72	0.13	0.15	0.28	0.13	0.19	0.19	0.17	0.19	212	10.0
9-25-72	0.12	0.11	0.12	0.10	0.14	0.15	0.16	0.15	240	20.6
9-26-72	0.14	0.13	0.13	0.08	0.10	0.08	0.07	0.12	164	20.8
9-27-72	0.09	0.38	0.14	0.12	0.12	0.13	0.11	0.10	120	15.6
9-28-72	0.12	0.10	0.13	0.13	0.15	0.13	0.11	0.15	76	13.9
9-29-72	0.11	0.09	0.09	0.08	0.08	0.08	0.09	0.09	12	17.2
10- 3-72	0.09	0.10	0.11	0.08	0.08	0.08	0.09	0.10	116	18.3
10- 4-72	0.11	0.13	0.16	0.10	0.09	0.09	0.10	0.12	120	16.4
10- 5-72	0.13	0.14	0.14	0.12	0.12	0.12	0.13	0.15	146	16.9
Unit No. 2										
10-11-72	0.65	0.85	0.76	0.84	1.03	1.02	0.95	1.21	680	12.8
10-13-72	1.13	1.07	1.00	0.90	1.05	1.10	1.07	1.00	730	4.4
10-16-72	1.60	1.40	1.35	1.35	1.27	1.60	2.80	3.35	1200	10.5
10-17-72	2.15	2.00	2.53	2.55	2.33	2.02	2.49	2.58	0	7.8
10-18-72	3.20	3.34	3.36	3.50	3.47	3.52	3.49	3.28	0	0.0
10-19-72	<b>1.</b> 60	<b>1.</b> 88	2.10	2.15	<b>1.68</b>	2.70	3.10	3.15	0	-0.3
10-20-72	2.44	2.98	2.85	2.80	3.05	2.40	2.70	2.55	0	2.8
10-25-72	2.10	1.75	1.80	2.10	<b>1.68</b>	<b>1.65</b>	<b>1.70</b>	<b>1.60</b>	0	6.1
10-27-72	2.53	2.55	2.15	2.34	1.91	2.10	<b>1.</b> 88	<b>1.</b> 68	0	7.5
10-30-72	3.20	3.50	3.25	2.60	3.31	3.42	3.54	3.32	0	3.3
0+eC	Τi	me and	Conce	ntrati	l ni nc	opm of \$	Sample	ß	Fan Operation	Average Temp.
------------	--------------	--------------	--------------	--------------	-------------	--------------	--------------	--------------	------------------	------------------
2	9 am	Noon	3 pm	6 pm	r mg 6	nidnight	3 am	6 am	Time (min).	(c)
Unit No. 1										
9-20-72	0.09	0.08	0.08	0.16	0.17	0.12	0.13	0.11	195	17.5
9-22-72	0.13	0.15	0.28	0.13	0.19	0.19	0.17	0.19	212	10.0
9-25-72	0.12	0.11	0.12	0.10	0.14	0.15	0.16	0.15	240	20.6
9-26-72	0.14	0.13	0.13	0.08	0.10	0.08	0.07	0.12	164	20.8
9-27-72	0.09	0.38	0.14	0.12	0.12	0.13	0.11	0.10	120	15.6
9-28-72	0.12	0.10	0.13	0.13	0.15	0.13	0.11	0.15	76	13.9
9-29-72	0.11	0.09	0.09	0.08	0.08	0.08	0.09	0.09	12	17.2
10- 3-72	0.09	0.10	0.11	0.08	0.08	0.08	0.09	0.10	116	18.3
10- 4-72	0.11	0.13	0.16	0.10	0.09	0.09	0.10	0.12	120	16.4
10- 5-72	0.13	0.14	0.14	0.12	0.12	0.12	0.13	0.15	146	16.9
Unit No. 2										
10-11-72	0.65	0.85	0.76	0.84	1.03	1.02	0.95	1.21	680	12.8
10-13-72	1.13	1.07	1.00	0.90	<b>1.05</b>	1.10	<b>1.</b> 07	<b>1.</b> 00	730	4.4
10-16-72	<b>1.</b> 60	<b>1.4</b> 0	<b>1.</b> 35	<b>1.</b> 35	1.27	<b>1.60</b>	2.80	3.35	1200	10.5
10-17-72	2.15	2.00	2.53	2.55	2.33	2.02	2.49	2.58	0	7.8
10-18-72	3.20	3.34	3.36	3.50	3.47	3.52	3.49	3.28	0	0.0
10-19-72	1.60	1.88	2.10	2.15	1.68	2.70	3.10	3.15	0	-0.3
10-20-72	2.44	2.98	2.85	2.80	3.05	2.40	2.70	2.55	0	2.8
10-25-72	2.10	<b>1.75</b>	1.80	2.10	<b>1.68</b>	<b>1.</b> 65	<b>1.</b> 70	<b>1.6</b> 0	0	6.1
10-27-72	2.53	2.55	2.15	2.34	1.91	2.10	1.88	<b>1.68</b>	0	7.5
10-30-72	3.20	3.50	3.25	2.60	3.31	3.42	3.54	3.32	0	а <b>.</b> З

APPENDIX B.--Sample Data for the Six Units Tested.

0 + -	н. Н	me and	Conce	ntrati	ni no	opm of	Sample	v v	Fan Operation	Average Temp.
המרפ	9 am	Noon	3 pm	g pm	n mg 6	uidnight	3 am	6 am	Time (min).	(c)
Unit No. 3										
11- 1-72	0.31	0.27	0.35	0.31	0.35	0.28	0.34	0.27	1121	5.6
11- 3-72	0.51	0.44	0.34	0.44	0.48	0.44	<b>D.</b> 48	0.44	1040	9.2
11- 6-72	0.34	0.25	0.31	0.28	0.34	0.31	0.33	0.28	1215	6.7
11- 7-72	0.46	0.38	0.34	0.33	0.34	0.38	0.48	0.56	1095	9.2
11- 9-72	0.34	0.33	0.34	0.43	0.31	0.59	0.43	0.34	1158	4.4
11-10-72	0.33	0.31	0.34	0.30	0.38	0.34	0.31	0.30	1260	5.0
11-13-72	0.33	0.30	0.32	0.42	0.35	0.38	0.35	0.38	666	2.8
11-15-72	0.35	0.37	0.37	0.35	0.32	0.47	0.40	0.35	240	-3.3
11-16-72	0.30	0.33	0.32	0.40	0.32	0.28	0.32	0.33	259	-6.4
11-17-72	0.31	0.38	0.30	0.44	0.33	0.30	0.35	0.30	272	-1.4
Unit No. 4										
11-29-72	0.94	0.64	0.57	0.74	0.59	0.80	<b>1.</b> 05	1.01	1440	-2.5
11-30-72	0.45	0.52	0.41	0.59	0.75	0.79	0.72	0.54	1440	0.0
12- 2-72	0.50	0.70	1.32	0.85	0.73	1.05	06.0	0.65	1440	-0.6
12- 4-72	0.73	0.54	0.53	<b>1.</b> 05	0.80	1.35	06.0	0.85	1440	-5.3
12- 8-72	0.62	0.58	0.63	0.52	0.88	0.75	0.65	0.60	1440	-6.9
12-11-72	0.85	0.50	0.87	1.42	1.35	1.15	<b>I.</b> 39	0.95	1440	-1.7
12-13-72	<b>1.</b> 05	0.85	0.87	0.73	0.85	1.52	1.40	1.16	1440	-1.1
12-15-72	0.93	0.81	1.49	1.58	1.22	1.40	1.17	<b>1.</b> 29	1440	-3.9
12-18-72	0.70	0.68	0.75	0.80	0.65	0.53	0.70	0.59	1440	- 3° 9
12-20-72	0.68	0.65	0.79	0.85	0.72	0.92	0.62	0.53	1440	0.8

APPENDIX B.--continued.

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Да+с П	Τi	ime and	l Conce	ntrati	on in	ppm of	Sample	Ŋ	Fan Operation	Average Temp.
	9 am	Noon	3 pm	e pm	md 6	midnight	3 am	6 am	Time (min)	(°C).
Unit No. 5										
12-22-72	0.22	0.12	0.18	0.12	0.10	0.17	0.15	0.19	1440	0.3
12-26-72	0.18	0.10	0.12	0.11	0.10	0.12	0.13	0.13	1440	0.0
12-27-72	0.13	0.12	0.11	0.13	0.14	0.12	0.13	0.12	1440	-2.5
12-28-72	0.14	0.12	0.10	0.15	0.11	0.13	0.14	0.15	1440	0.1
<b>1-</b> 2-73	0.15	0.14	0.13	0.14	0.12	0.10	0.15	0.13	1440	-1.8
1- 4-73	0.16	0.12	0.14	0.12	0.13	0.11	0.13	0.14	1440	0.3
I- 5-73	0.12	0.13	0.12	0.10	0.13	0.14	0.13	0.15	1440	-6.7
<b>1-</b> 9-73	0.14	0.10	0.12	0.14	0.11	0.13	0.14	0.10	1440	-9.2
1-10-73	0.10	0.12	0.09	0.11	0.08	0.10	0.11	0.12	1440	-10.6
1-11-73	0.11	0.12	0.10	0.08	0.11	0.10	0.12	0.12	1440	-9.7
Unit No. 6										
	с г с	(  - 	r c	C T C	r c	r c	( 7	(  - 	c r [	( (
1-22-73	0.10	0.13	0.14	0.12	0.14	0 • 14	0.16	0.13	710	m   m
1-24-73	0.10	0.11	0.12	0.11	0.12	0.11	0.09	0.10	740	-1.1
1-25-73	0.13	0.12	0.14	0.16	0.14	0.14	0.14	0.11	510	3 <b>.</b> 9
<b>1-29-73</b>	0.15	0.14	0.12	0.10	0.11	0.12	0.15	0.15	345	-7.5
1-30-73	0.13	0.15	0.14	0.16	0.14	0.16	0.15	0.14	115	-4.4
1-31-73	0.12	0.11	0.13	0.11	0.11	0.12	0.11	0.10	485	-3.6
2- 1-73	0.10	0.12	0.10	0.11	0.10	0.11	0.12	0.09	370	2.8
2- 6-73	0.09	0.11	0.10	0.12	0.11	0.12	0.11	0.10	385	1.1
2- 8-73	0.11	0.12	0.10	0.09	0.12	0.10	0.11	0.10	350	-7.5
2-11-73	0.12	0.10	0.11	0.12	0.11	0.13	0.10	0.12	275	-11.4
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APPENDIX B.--continued.

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