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# A Study of the Gas-Solid Reaction Between Hydrogen Sulfide and Mercury(I) Chloride; Development of a Method for Determination of Atmospheric Hydrogen Sulfide

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A STUDY OF THE GAS-SOLID REACTION BETWEEN  
HYDROGEN SULFIDE AND MERCURY(I) CHLORIDE;  
DEVELOPMENT OF A METHOD FOR  
DETERMINATION OF ATMOSPHERIC HYDROGEN SULFIDE

by

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B.S. March 1975, Florida Institute of Technology  
Melbourne, Florida

A Thesis Submitted to the Faculty of Old Dominion  
University in Partial Fulfillment of the  
Requirements for the Degree of

MASTER OF SCIENCE

CHEMISTRY

OLD DOMINION UNIVERSITY  
December 1977

Approved by:

~~B. T. Upchurch~~ (Director)

R. A. Pal

## ABSTRACT

### A STUDY OF THE GAS-SOLID REACTION BETWEEN HYDROGEN SULFIDE AND MERCURY(I) CHLORIDE; DEVELOPMENT OF A METHOD FOR DETERMINATION OF ATMOSPHERIC HYDROGEN SULFIDE

Eric H. De Carlo  
Old Dominion University, 1977  
Director: Dr. B. T. Upchurch

The possibility of measuring hydrogen sulfide indirectly by measuring the mercury evolved from the gas-solid reaction between hydrogen sulfide and mercury(I) chloride was studied. DMCS treated glass wool was coated with mercurous chloride and used as a conversion material. The response to hydrogen sulfide was studied as a function of concentration and temperature. The possible interference of other sulfur gases and water was examined.

The studies indicated that hydrogen sulfide could be determined at concentrations as low as 15 ppb. It was found that mercaptans would actively interfere with the hydrogen sulfide to mercury conversion, but that sulfur dioxide would not interfere even in large concentrations. Water was found to interfere by causing the decomposition of the mercurous chloride coated on the support. The time constant of the system was found to be small enough to permit monitoring on a real time basis.

## ACKNOWLEDGMENTS

Acknowledgment is given to Robert Work for construction of the glassware necessary for these studies.

The writer would like to express his thanks to the director of research, Dr. B. T. Upchurch, for his guidance and support during the course of this investigation.

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## CHAPTER I

### INTRODUCTION

#### Hydrogen Sulfide, Present Methods of Determination

Hydrogen sulfide, a toxic gas often found polluting our environment, is also very malodorous and corrosive. Low concentrations may affect the nervous system while higher concentrations can cause fatalities. It is released into the atmosphere by the anaerobic digestion of various industrial wastes from refineries, petrochemical works, and oil fields. It is a by-product in the production of heavy water, synthetic fibers, and paper. Ambient levels of hydrogen sulfide are in the parts per billion range. Occupational Safety and Health Administration (OSHA) has set general standards for industry for hydrogen sulfide, methyl mercaptan, and sulfur dioxide in the parts per million (ppm) range (24, 25).<sup>1</sup> Concentrations as high as 200ppm have been observed during oil drilling operations.

There are many methods available for the determination of hydrogen sulfide, but most of these methods are either grab sample techniques, which do not permit real time monitoring, or methods which do not have the sensitivity needed to measure hydrogen sulfide at OSHA levels. A standard method for environmental samples involves the collection of the hydrogen sulfide by passage through a cadmium hydroxide suspension followed by reaction with para-amino N,N dimethylaniline to form

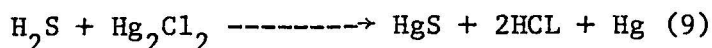
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<sup>1</sup>Maximum exposure to these gases was set at 10 ppm for methyl mercaptan, 5 ppm for sulfur dioxide and 20 ppm for hydrogen sulfide. (At 25°C and 760 mm Hg)

Methylene blue (1, 7, 11). The most common methods used involve the reaction of hydrogen sulfide with lead acetate tape to form a brown stain of lead sulfide (13, 16). A photocell detects the loss in reflected light which is directly proportional to the hydrogen sulfide concentration (5). Other methods include tape covered with mercuric chloride (6), potassium dicyanoargentate (13), or silver nitrate (12). A more precise method uses gas chromatography with a flame photometric detector; however this is limited in application by its inability to monitor continuously and by the bulk of hardware needed for the analysis. This method is usually used for analysis of trace levels of sulfur compounds in the gases analyzed (2, 21, 22, 23). In the past few years several other methods have appeared. Kiba and Furusawa describe a sensor for hydrogen sulfide based on the catalytic effect of the gas on the iodine azide reaction (8). This method uses flowing sample streams and has a detection limit of 5 ng with a relative standard deviation of  $\pm 10\%$ . A method for electrochemical determination of hydrogen sulfide in air has been proposed by Sedlak and Blurton which is based on the electrochemical oxidation of hydrogen sulfide at a Teflon bonded diffusion electrode (17, 18). Another method, though of low sensitivity, uses Palladium Insulated Gate Field Effect Transistors and functions due to the spontaneous dissociation of hydrogen sulfide into hydrogen and sulfur atoms on palladium at room temperature (19). The hydrogen atoms are transported across the palladium film and are adsorbed onto the palladium-silicon dioxide interface thus changing the threshold voltage. The sensitivity permits detection of the gas in the parts per million range.

### Proposed Investigation

If the well known solution reaction between hydrogen sulfide and mercury(I) can be shown to occur as a gas-solid reaction then the possibility of measuring hydrogen sulfide indirectly would be demonstrated.

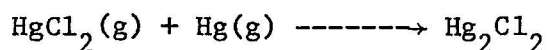


From the stoichiometry of the reaction a measure of the amount of evolved mercury would give a measure of the hydrogen sulfide initially present. With renewed efforts in pollution control has come a need for monitoring hydrogen sulfide at the parts per million level and lower. Since the flameless atomic absorption detection limit for mercury has been established at less than .001  $\mu\text{g}$  (10), similar levels of hydrogen sulfide undergoing the above reaction could be detected indirectly.

It was proposed that, by passing a stream of air containing hydrogen sulfide over a high surface area solid support coated with mercurous chloride, the above reaction would occur. The evolved elemental mercury could then be monitored by the use of cold vapor atomic absorption. Hydrogen sulfide permeation tubes would be used as a source of known concentrations of hydrogen sulfide. Since water vapor has been reported to cause the decomposition of mercurous chloride (9), the effects of water would be studied. The possible interference by other sulfur containing gases, (sulfur dioxide and lower alkyl mercaptans), on the reaction would be examined. Due to preliminary studies showing that an increase in temperature caused an increase in the rate of the reaction between hydrogen sulfide and

mercurous chloride, a study of the reaction as a function of temperature would be done. Duval reported calomel to be stable in a dry atmosphere up to a temperature of 130°C (after which it began to decompose) (4).

Mercurous chloride would be coated onto a high surface solid support by first coating the beads with mercuric chloride followed by reduction to the mercurous salt. Sublimation of mercuric chloride and elemental mercury are known to react to form mercurous chloride (9) by the following reaction:



Other methods for preparing the reagent coating would be investigated if needed.

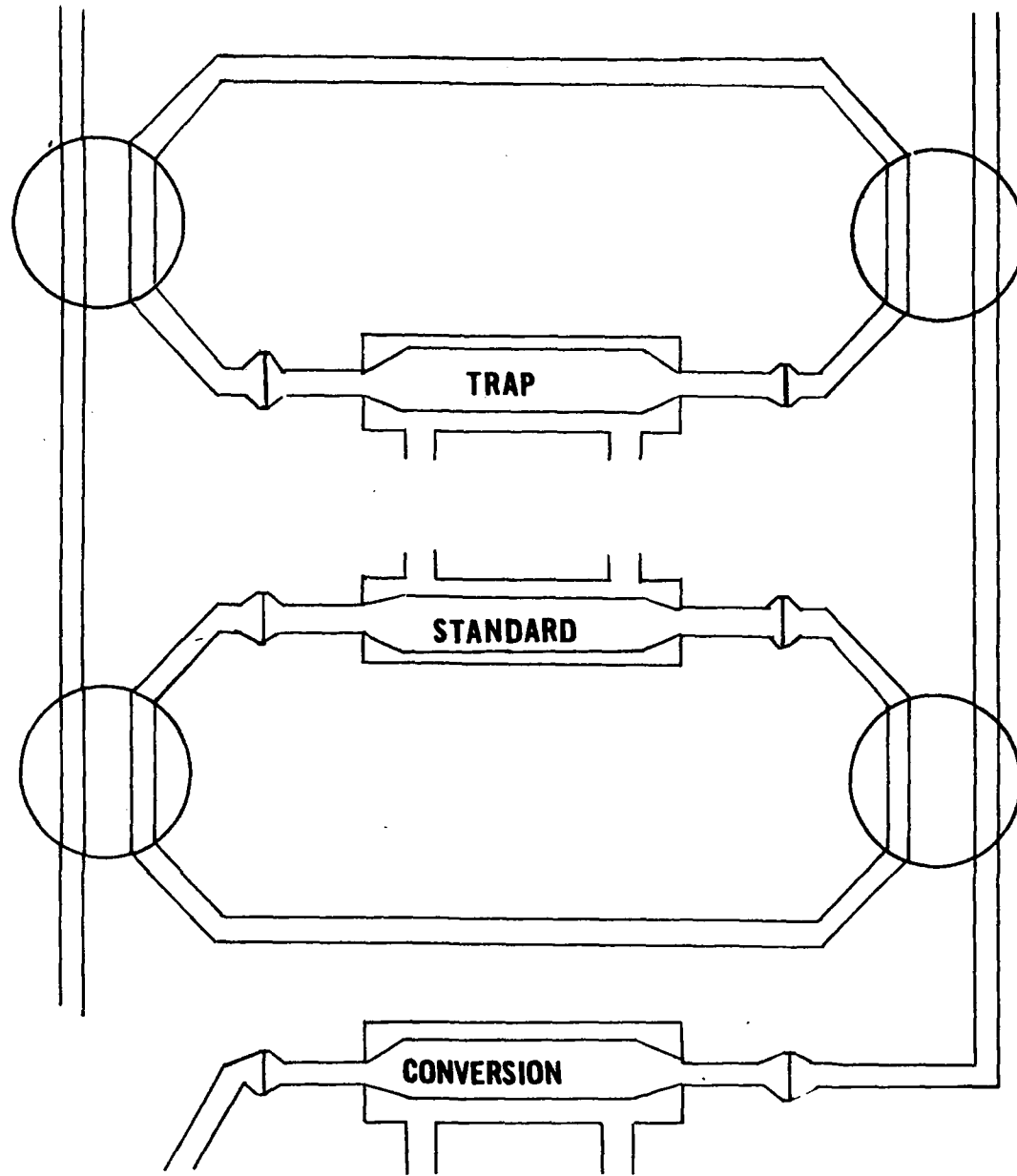
## CHAPTER II

### EXPERIMENTAL

#### Apparatus and Materials

All absorption measurements were made at 253.65 nm on a Perkin-Elmer Coleman 50 mercury analyzer system equipped with a Houston Instrument Omniscribe potentiometric chart recorder. The sensitivity of this instrument is in the range of .01  $\mu$ g of mercury. A Brooks Instrument Division digital flow meter was used for all flow measurements. Temperature control was maintained within .1°C using a Forma Scientific model Forma-Temp Jr. bath and circulator.

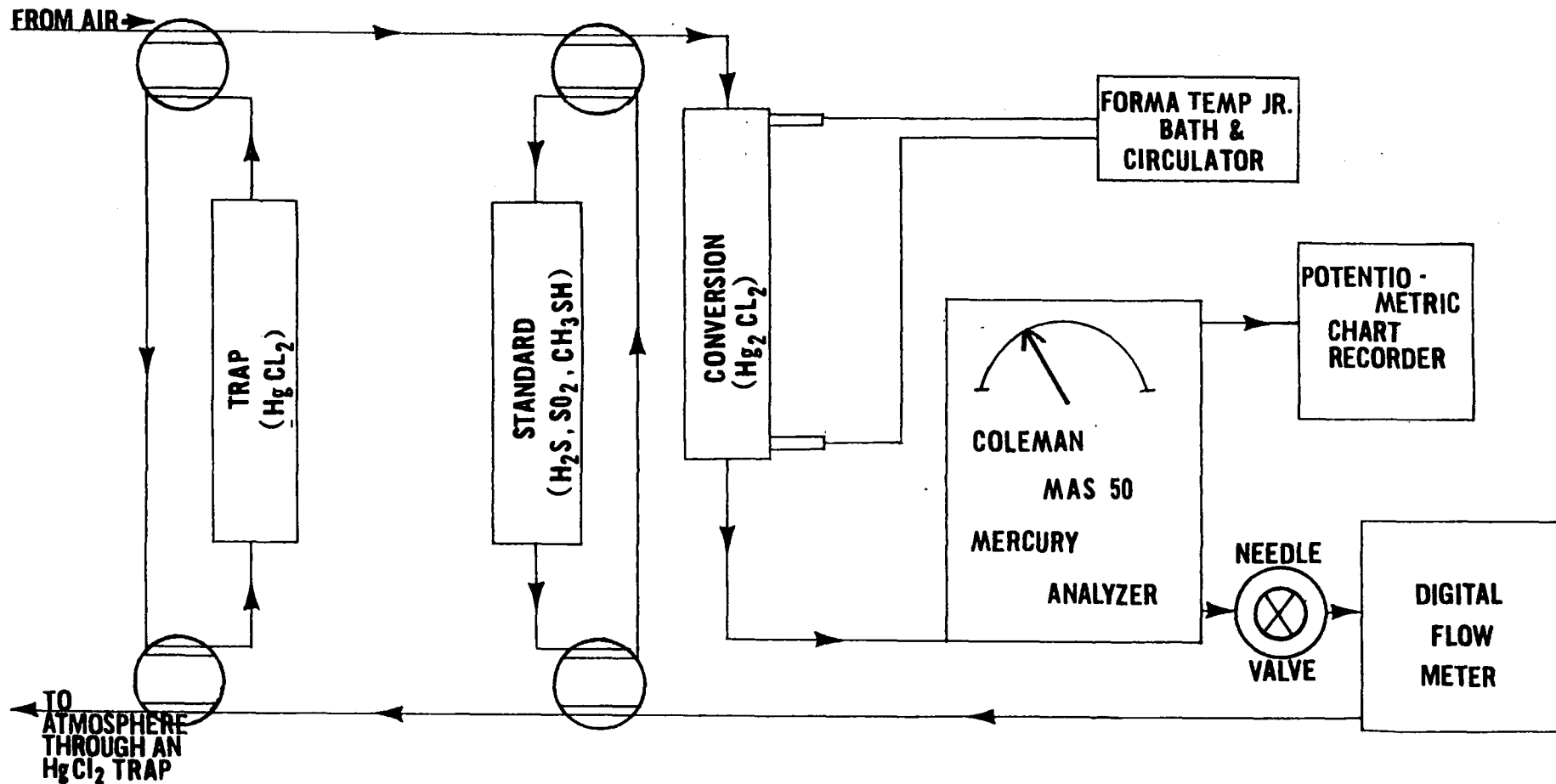
All chemicals used were of reagent quality. The mercurous and mercuric chloride were obtained from Mallinckrodt Chemical Works and Fisher Scientific Company, respectively. The anhydrous ether used was also from the Mallinckrodt Chemical Works. Standard gas permeation tubes and wafers for hydrogen sulfide, methyl mercaptan, and sulfur dioxide were purchased from Metronics Associates Incorporated. Porasil C porous-silica beads (80-100 mesh), DMCS treated glass wool, as well as DMCS treated glass beads (80-100 mesh) were obtained from Alltech Associated Incorporated. The Chromosorb A-NAW (60-80 mesh) used came from Analabs Incorporated. Carrier gases (Nitrogen and Helium) were obtained from the Linde Corporation. Special glass apparatus used in these studies was designed in the laboratory and constructed by Modern Machine and Tool Company, Newport News, Virginia. The glass apparatus shown in Figure 1 was designed with four way valves in order to



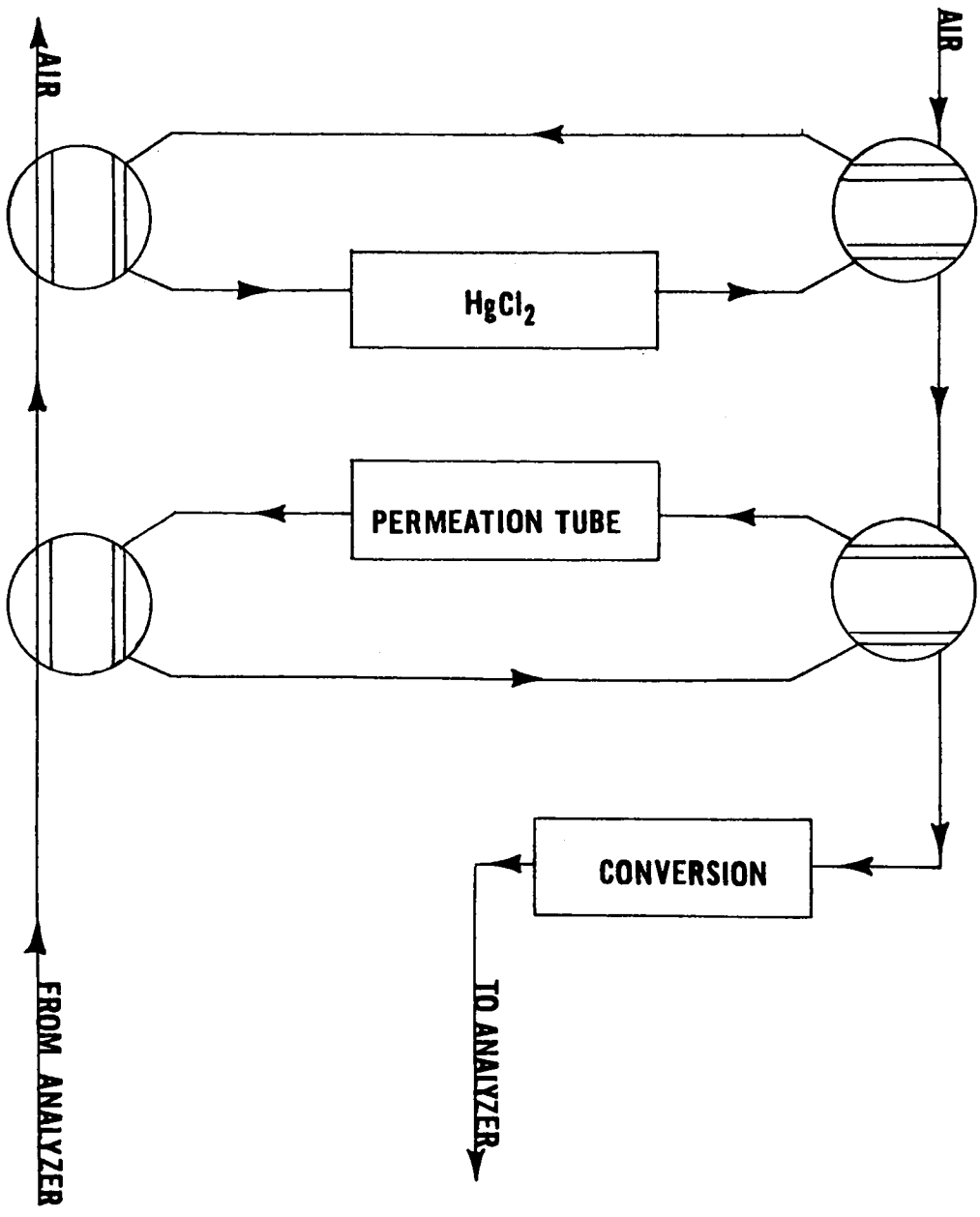
accommodate calibrate, zero, and measuring modes. A block diagram of the complete experimental set up is shown in Figure 2. Connections between components were made with Tygon tubing in order to minimize the chance of adsorption on the tubing walls. Diagrams of the configurations required for each mode of operation are shown in Figures 3, 4, and 5.

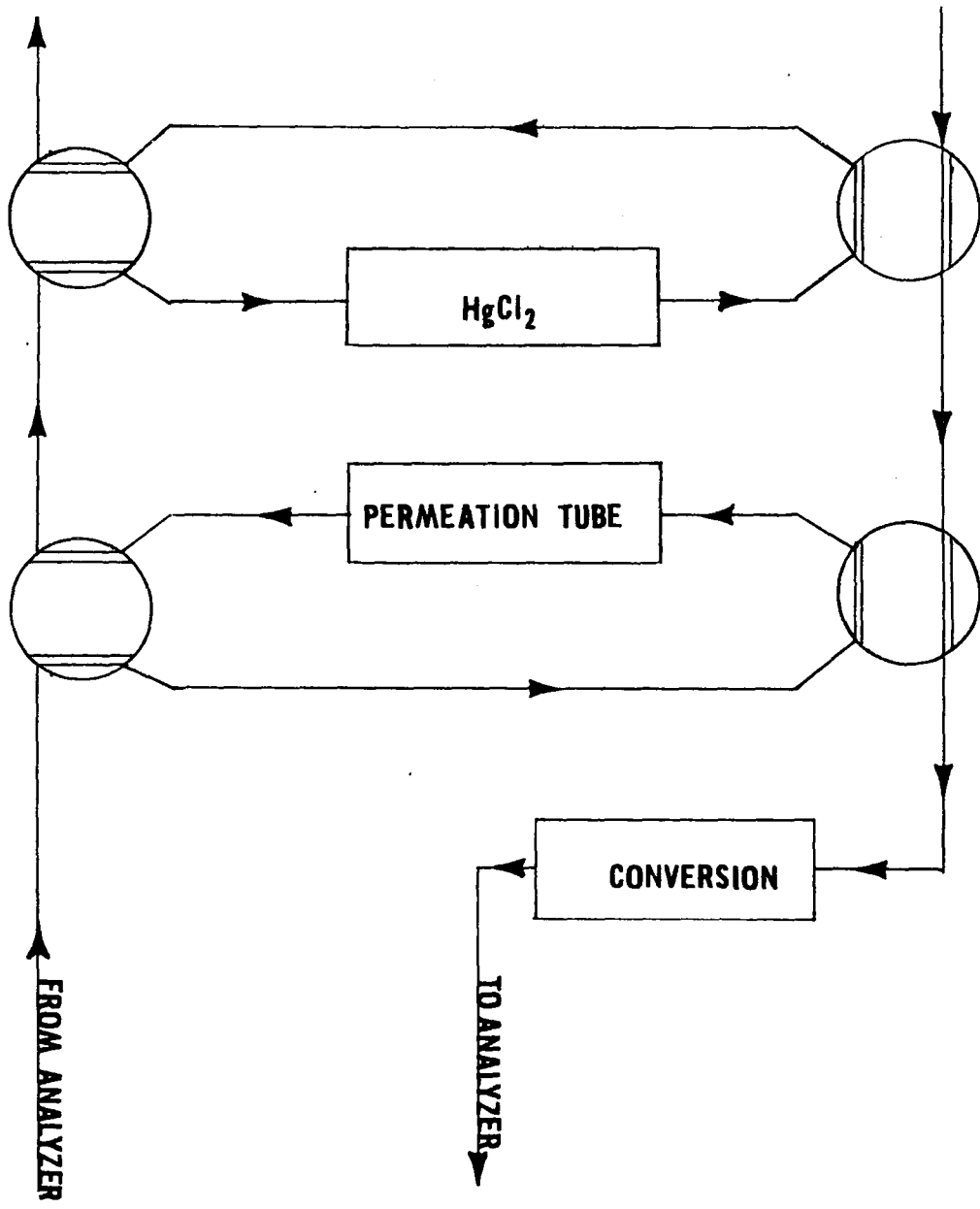
#### Preparation of a Mercurous Chloride Coating on a High Surface Area Solid Support

A known amount of Porasil C glass beads was dried in the oven at 110°C for three hours. The dried beads were then immersed in an aqueous solution of saturated mercuric chloride. After immersion the beads were vacuum filtered and dried in a desiccator filled with anhydrous magnesium perchlorate for 24 hours. The loading on the beads was determined by weighing a portion of the dried beads followed by washing them free of the mercuric chloride that had been adsorbed and then reweighing after drying. By this method loadings from three to twelve per cent were obtained. The reduction of the mercuric chloride on the beads was attempted by placing the coated beads in a Thiele tube with a stoichiometric quantity of elemental mercury and sealing the whole under a vacuum. The apparatus was then placed in the oven at 250°C to effect the reduction. The high temperature was used in order to increase the vapor pressure of the mercury to an acceptable level. The vapor pressure of mercury at 24°C is  $1.69 \times 10^{-3}$  mm Hg while at 250°C it is 74.375 mm Hg (26). The experimental set up used in this method is shown in Figure 6. This method however proved to be unacceptable as the high temperatures under vacuum caused









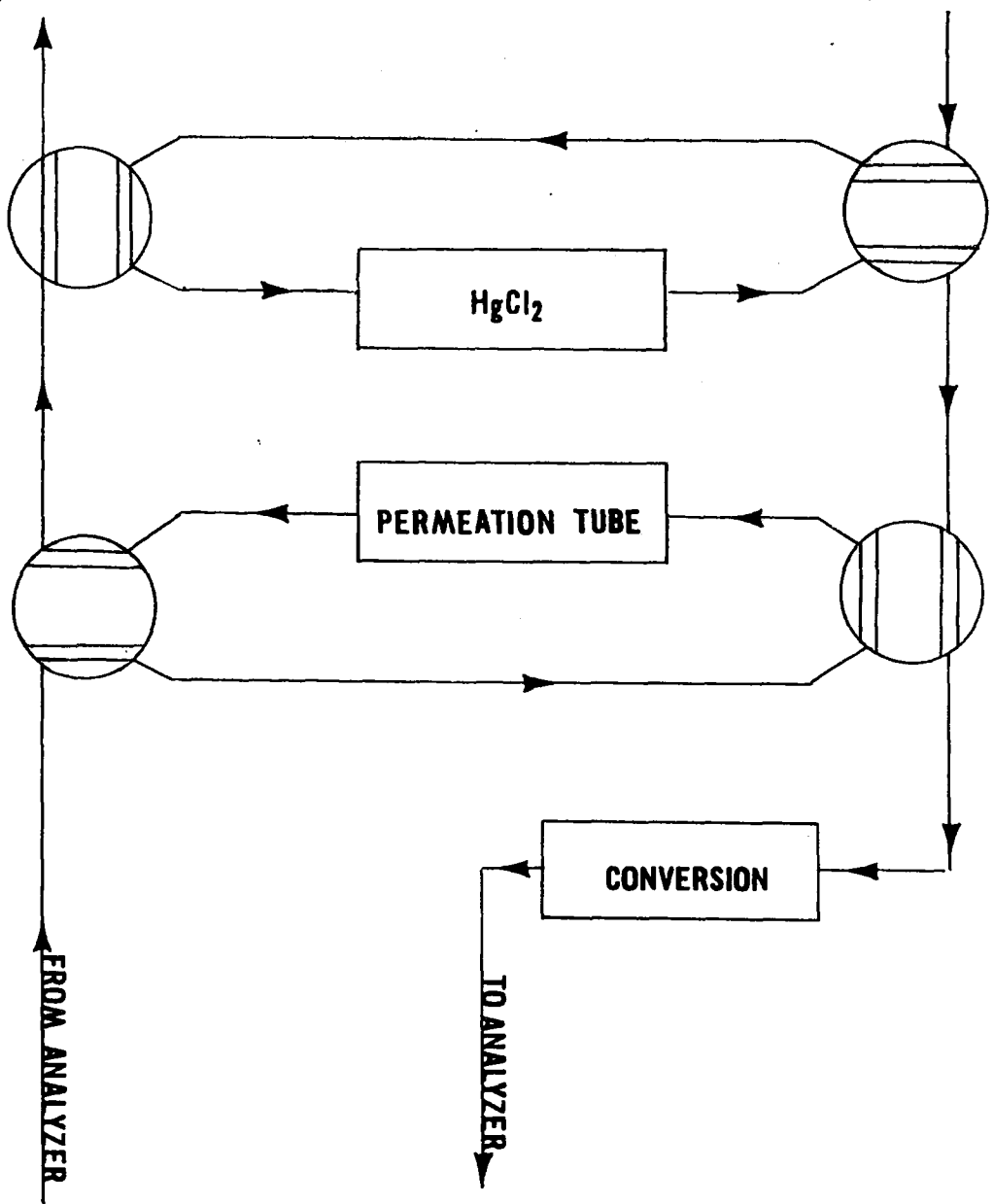
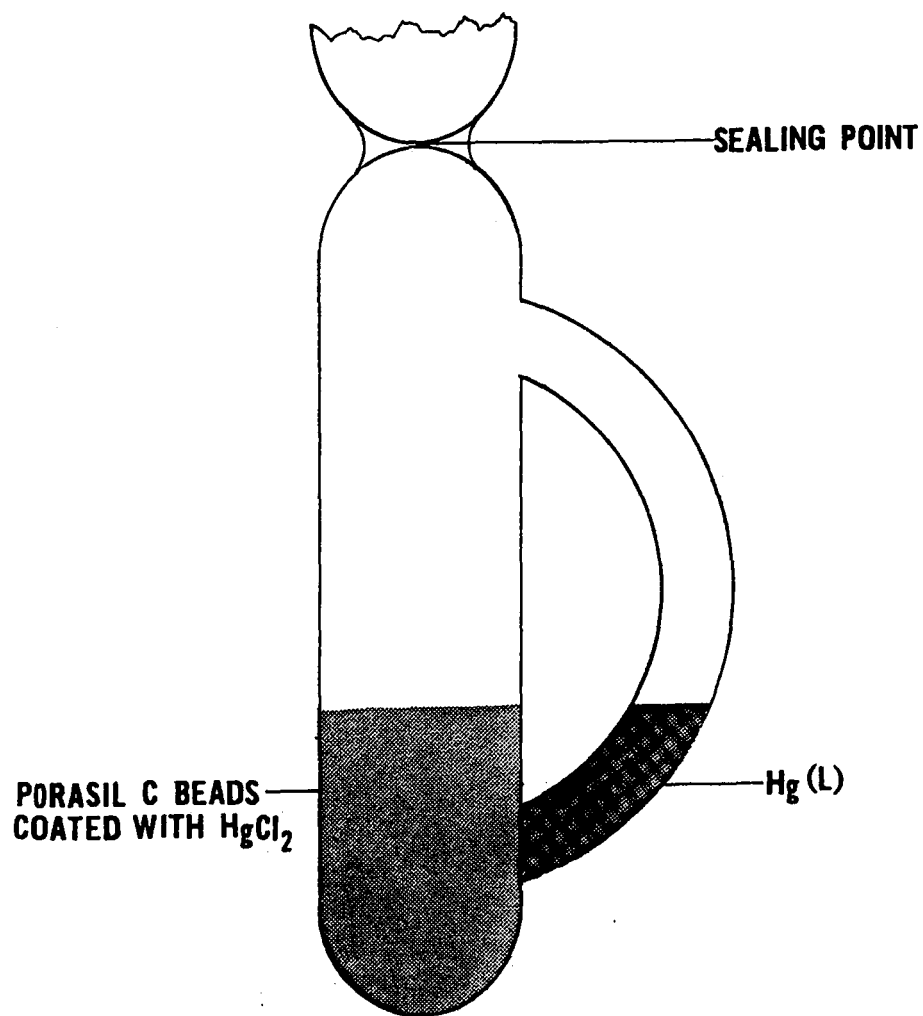


FIGURE 6

APPARATUS FOR REDUCTION OF MERCURIC CHLORIDE  
TO MERCUROUS CHLORIDE



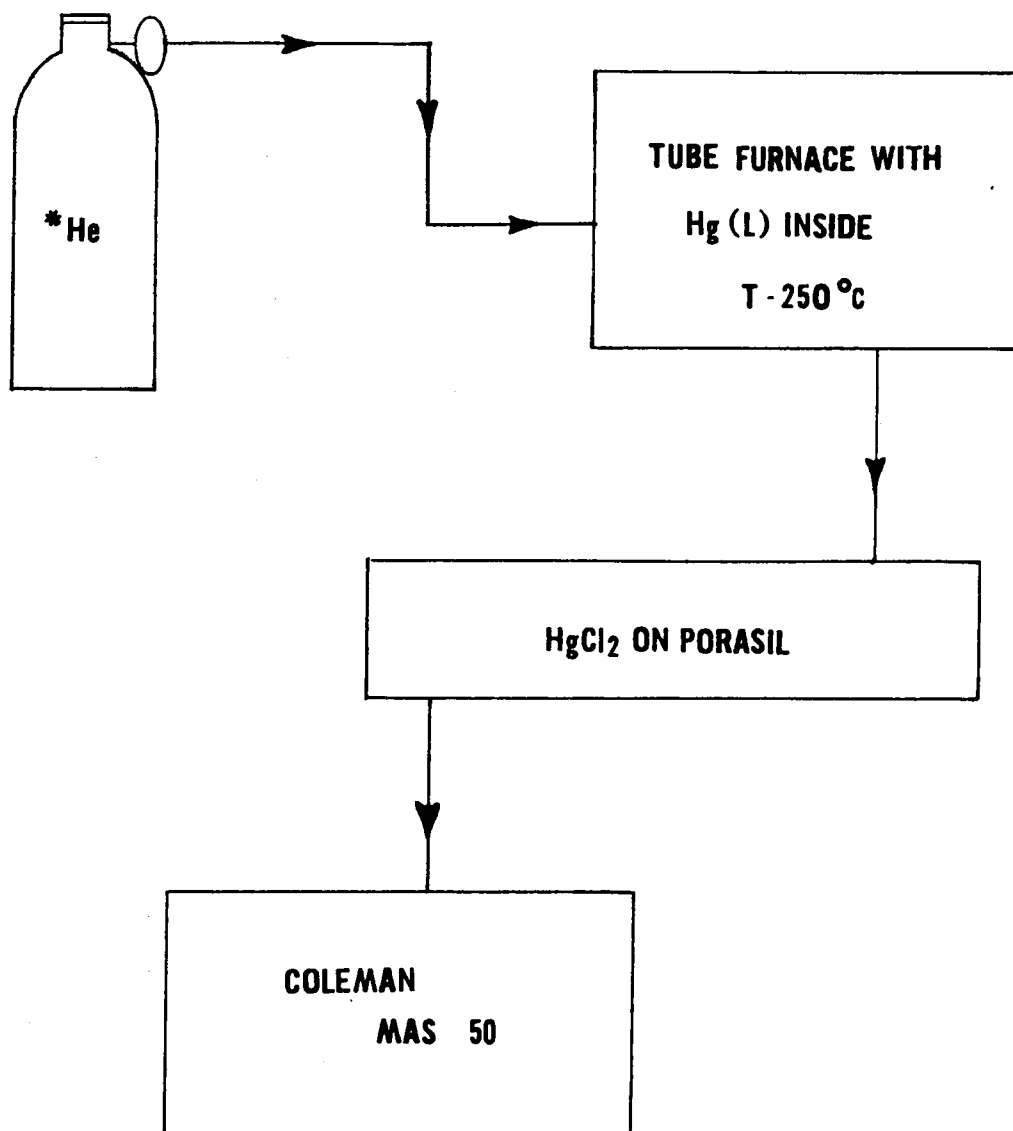
sublimation of the mercurous chloride from the solid support as soon as it was formed.

The reduction of the mercuric chloride was attempted another way. This time only the elemental mercury was heated and the mercury vapor drawn over the beads coated with the mercuric salt under helium flow. The mercury analyzer was attached to the other end. It was anticipated that when the mercuric salt had all been converted to the mercurous form the analyzer would detect elemental mercury getting past the solid support. As long as all the mercuric salt had not been reduced there should be no elemental mercury detected at the instrument. A diagram for this is shown in Figure 7. Problems were encountered with this method as the mercury vapor never passed over the Porasil beads but instead condensed at the front of the column. Attempts were made to purge out the excess mercury by passing a stream of heated gas over the beads and condensed mercury. This configuration differed from the one shown in Figure 7 only in as much as the mercury in the oven had been removed. This process was too slow to be useful. The method was again altered so that both the beads and the mercury were held at 100°C in an oven. It was hoped that in this way sublimation and condensation problems on the beads would be avoided and reduction to the mercurous chloride would proceed. This was found to be extremely slow as the excess mercury remained on the beads for very long periods of time rendering the method ineffective.

In order to avoid drying the beads in the oven after coating, and hoping to avoid sublimation problems, an attempt was made to coat the beads by slurring the Porasil support with a saturated solution of

FIGURE 7

BLOCK DIAGRAM FOR REDUCTION OF MERCURIC CHLORIDE



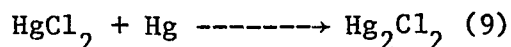
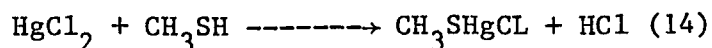
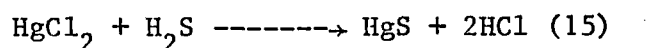
**\* N<sub>2</sub> WAS ALSO USED WHEN He WAS UNAVAILABLE**



mercuric chloride in anhydrous ether and evaporating the solvent under nitrogen flow to avoid water formation during the evaporation. It has been reported that six grams of mercuric chloride are soluble in 100 ml of di-ethyl ether (20). Loadings on the order of two per cent were achieved in this manner. Conversion to the mercurous salt was then attempted in a similar manner as before except at room temperature. Again this was too slow to be useful. Another process attempted involved stirring the beads and mercuric chloride in a slurry with ether and then adding slightly less than a stoichiometric amount of elemental mercury by means of a fine capillary. It was believed that this would cause the Porasil beads to act as nucleating sites for the mercurous chloride resulting from the redox reaction between elemental mercury and the mercuric chloride. The slurry was then stirred until the solvent evaporated. The Porasil beads were put in a glass column and washed with ether to remove any excess mercuric chloride and then dried under nitrogen flow. To insure that there was no moisture in the gas it was passed through a drying tube filled with magnesium perchlorate. By this method the Porasil C beads were coated with 2.5 per cent mercurous chloride by weight.

#### Preparation of a Scrubbing Material

Before any conversion studies could be done it was necessary to make a scrubbing material to remove mercury, hydrogen sulfide, lower alkyl mercaptans, and any other interfering sulfur containing gases that might be present in the air streams used. The following reactions are known to occur in solution; in this work it was also found that they proceed as gas-solid reactions.



A solid support coated with the mercuric salt would then stop both the mercury, the hydrogen sulfide, and the mercaptans. To make the trap Chromosorb A-NAW was coated by slurring in a saturated solution of mercuric chloride in anhydrous ether and evaporating off the solvent. Loadings of four per cent were achieved.

Hydrogen Sulfide - Mercury Conversion  
as a Function of Temperature

The apparatus shown in Figure 1 was set up for operation. The trap was filled with one inch of Chromosorb A-NAW coated with mercuric chloride, and the conversion tube was filled with one inch of Porasil C coated with mercurous chloride. The loadings for the trap and the conversion materials were 4.16% and 2.55% respectively. A study of the response signal observed for a scrubbed air sample was performed as a function of temperature. This was effectively a measure of the evolved mercury from the conversion material as its temperature was raised. Along with this a study of the response observed for a fixed concentration of hydrogen sulfide as a function of temperature was performed. The fixed concentration of hydrogen sulfide was obtained by letting the gas permeate from the tube at the rate dictated by its temperature. A two centimeter tube was used and the temperature was held at 23°C. At this temperature the two centimeter tube released 500 ng of hydrogen sulfide per minute. During the above studies the air stream drawn from the room was constantly passed through the

mercuric chloride trap in order to remove any mercury, hydrogen sulfide, as well as any other sulfur containing gas that might be present. Flow through the system was maintained at a constant rate during the studies. The data obtained is shown in Table I.

TABLE I: TEMPERATURE STUDIES

TEMPERATURE (°C)	ABSORBANCE (a)	ABSORBANCE (b)
30	0.018	0.061
32	0.022	0.071
35	0.027	0.081
37	0.027	0.092
40	0.032	0.108
42	0.034	0.125
45	0.041	0.155
47	0.046	0.187
50	0.061	0.222
52	0.071	-
55	0.086	-

(a) Response observed for scrubbed air without hydrogen sulfide

(b) Response observed for 14.73 nmole/minute  $H_2S$  drawn through system

Graphical representation of the above data is shown in Figure 8. In the above studies only the temperature of the conversion tube was varied.

During the temperature study of response to a fixed concentration of hydrogen sulfide it was noticed that although response to the gas

FIGURE 8

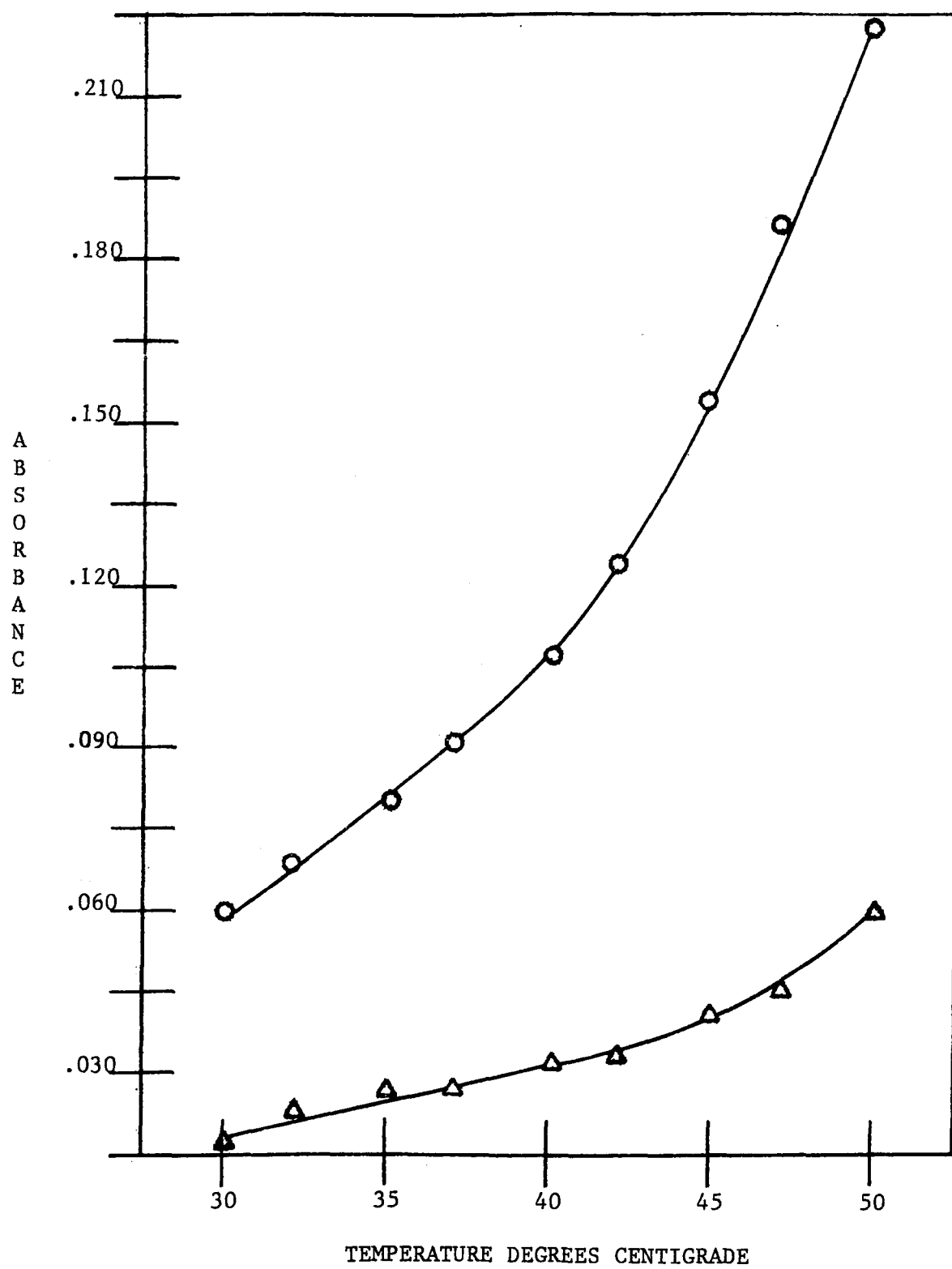
PLOT OF ABSORBANCE VERSUS TEMPERATURE FOR

○ A FIXED CONCENTRATION OF HYDROGEN SULFIDE

AND

△ IN THE ABSENCE OF HYDROGEN SULFIDE

## ABSORBANCE VERSUS TEMPERATURE



was fairly fast, the return to background levels took quite some time (five to twenty minutes). Because of this slow return time it was decided to do a study of the return to background time as a function of the conversion tube temperature. The slow return was noticed when the absorbance did not decrease immediately after shutoff of the hydrogen sulfide supply. At room temperature (23°C) the return to background was too slow to achieve effective real time monitoring. The conversion tube temperature was raised by five degree increments and the return time observed for fixed levels of hydrogen sulfide. Temperature control was accomplished by passing warm water from the bath and circulator around the conversion tube as had been done previously in the response studies. During this study the hydrogen sulfide concentration was permitted to buildup in the tube containing the permeation device. The gas was then released into the conversion tube by flushing it with a clean air stream for five to eight seconds. The instrument flow was kept at 200 ml/minute. Buildup times varied slightly from run to run but were such that the response initially observed would reach near full scale (zero to 25% transmittance). Two sets of data were obtained at 30°C and 35°C, and three sets were obtained for 40°C, 45°C, and 50°C. The data were averaged and are shown in Tables II and III.

TABLE II: RESPONSE STUDIES

ABSORBANCE (c)	TIME (sec) AT 30°	TIME (sec) AT 35°
1.000	3 (a)	0 (b)
0.699	16	8
0.602	19	14

TABLE II (continued)

ABSORBANCE (c)	TIME (sec) AT 30°	TIME (sec) AT 35°
0.456	42	27
0.347	71	49
0.301	93	68
0.260	118	91
0.222	155	124
0.187	209	171
0.155	283	247
0.125	409	380
0.097	634	584
0.071	990	1033

(a) Signal initially observed for the 30°C run was 1.097 on the absorbance scale.

(b) Signal initially observed for the 35°C run was 1.000 on the absorbance scale.

(c) The time shown in the table is the time elapsed before the signal returned to the absorbance value shown at the specified temperature setting.

(d) Temperature of the permeation tube was held at 24°C which is equivalent to a permeation rate of 16.08 nmole/min.

TABLE III: RESPONSE STUDIES

ABSORBANCE (a)	TIME (sec)		
	40° (b)	45° (c)	50° (d)
1.000	-	1	-
0.699	0.5	3	-
0.602	1	5	2
0.456	4	9	5
0.347	7	15	11
0.260	12	23	29
0.187	32	54	75
0.125	72	127	297
0.097	270	260	-

(a) The time shown in the table is the time elapsed before the signal returned to the absorbance value shown at the specified temperature.

TABLE III: (continued)

- 
- (b) Initial signal observed at 40°C was 0.721 on the absorbance scale.
  - (c) Initial signal observed at 45°C was 1.045 on the absorbance scale.
  - (d) Initial signal observed at 50°C was 0.730 on the absorbance scale.
  - (e) Temperature of the permeation tube was held at 24°C which is equivalent to a permeation rate of 16.08 nmole/min.
- 

It was noticed that at temperatures of 50°C and higher the return time increased drastically instead of decreasing as had been the case between 30°C and 50°C. Very high absorbance values were obtained even in cases where the hydrogen sulfide had been shut off. This would seem to indicate that at those temperatures the conversion material was releasing elemental mercury or decomposing. Figure 9 shows the return times for the various temperatures studied.

#### Response of Hydrogen Sulfide as a Function of Concentration

Response studies were done as a function of the hydrogen sulfide concentration to see if the Beer-Lambert law was being followed. Since the permeation tubes give off the gases at a constant rate (for a given temperature) it was necessary to develop a method of changing the concentration of the hydrogen sulfide reaching the conversion tube. This was done by the use of a needle valve controlling the flow through the system. Varying the flow rate varied the concentration as is shown by the following equation:

$$C = \frac{Pr}{MW \cdot F}$$

where C is concentration in nanomoles per milliliter, Pr is the permeation rate in nanograms per minute, MW is the molecular weight of the gas in nanograms per nanomole, and F is the flow rate through



FIGURE 9

PLOT OF ABSORBANCE VERSUS TIME FOR HYDROGEN SULFIDE

■ AT 30° C

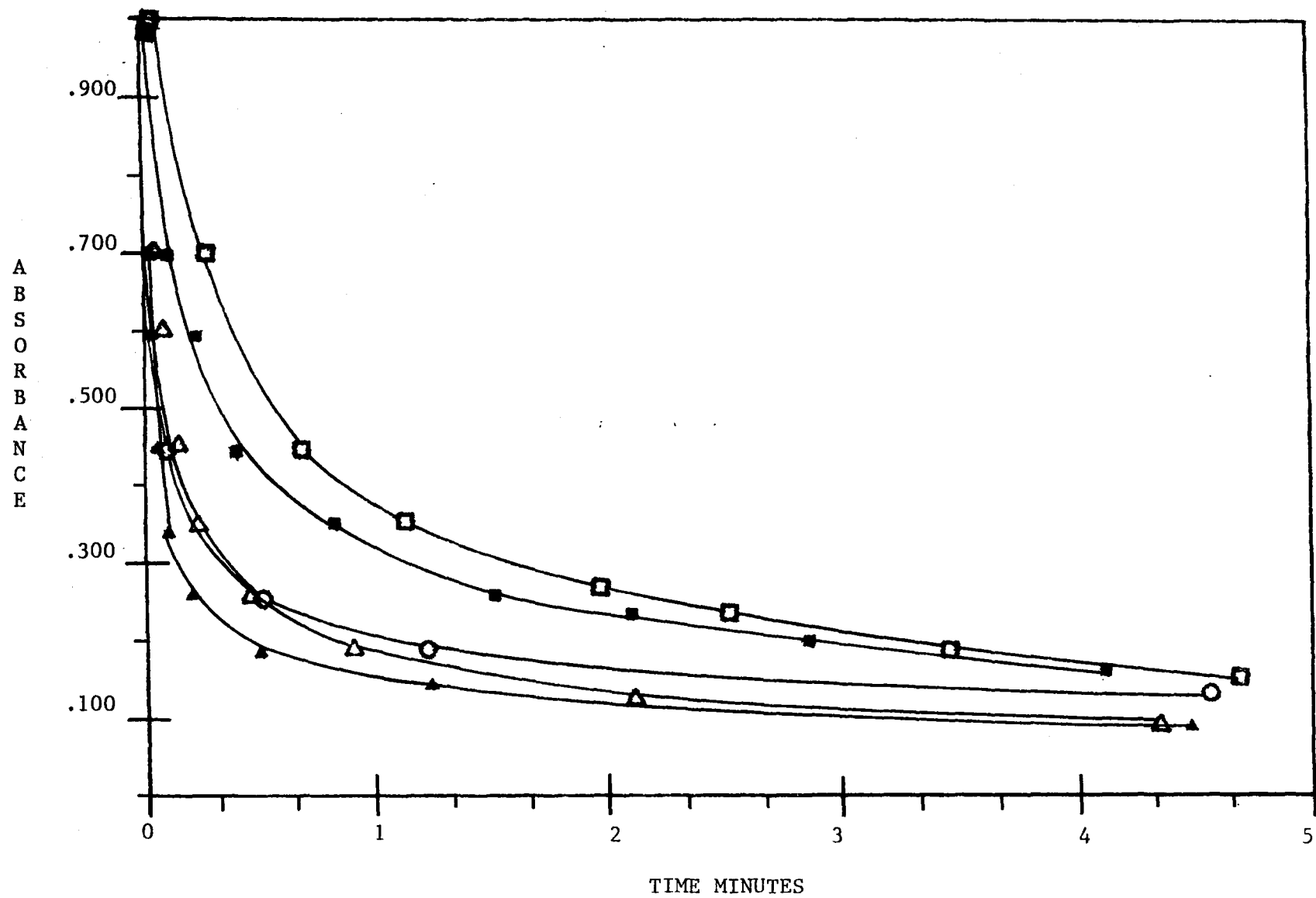
■ AT 35° C

▲ AT 40° C

△ AT 45° C

○ AT 50° C

# ABSORBANCE VERSUS TIME



the apparatus in milliliters per minute. Permeation for the hydrogen sulfide tube was determined from information given by the manufacturer and is shown in Figure 10. The data obtained in the concentration studies is shown in Table IV and Figure 11. These data were obtained by permitting the hydrogen sulfide to flow over the conversion material at a known flow rate. Sufficient time to equilibrate at the particular flow rate was allowed to insure steady state conditions.

TABLE IV: CONCENTRATION STUDIES

FLOW RATE (ml/min)	ABSORBANCE (a)	(H <sub>2</sub> S) (nmole/ml)
200	0.168	$8.79 \times 10^{-2}$
190	0.178	$9.25 \times 10^{-2}$
180	0.193	$9.77 \times 10^{-2}$
170	0.205	$1.03 \times 10^{-1}$
160	0.215	$1.10 \times 10^{-1}$
150	0.231	$1.17 \times 10^{-1}$
141	0.242	$1.25 \times 10^{-1}$
130	0.257	$1.35 \times 10^{-1}$
119	0.281	$1.48 \times 10^{-1}$
109	0.305	$1.61 \times 10^{-1}$
101	0.330	$1.74 \times 10^{-1}$
90	0.362	$1.96 \times 10^{-1}$
79	0.401	$2.20 \times 10^{-1}$
69	0.453	$2.53 \times 10^{-1}$
60	0.499	$2.93 \times 10^{-1}$
49	0.578	$3.59 \times 10^{-1}$

FIGURE 10

PLOT OF TEMPERATURE VERSUS LOG PERMEATION RATE  
PER CENTIMETER OF TUBE LENGTH FOR HYDROGEN SULFIDE

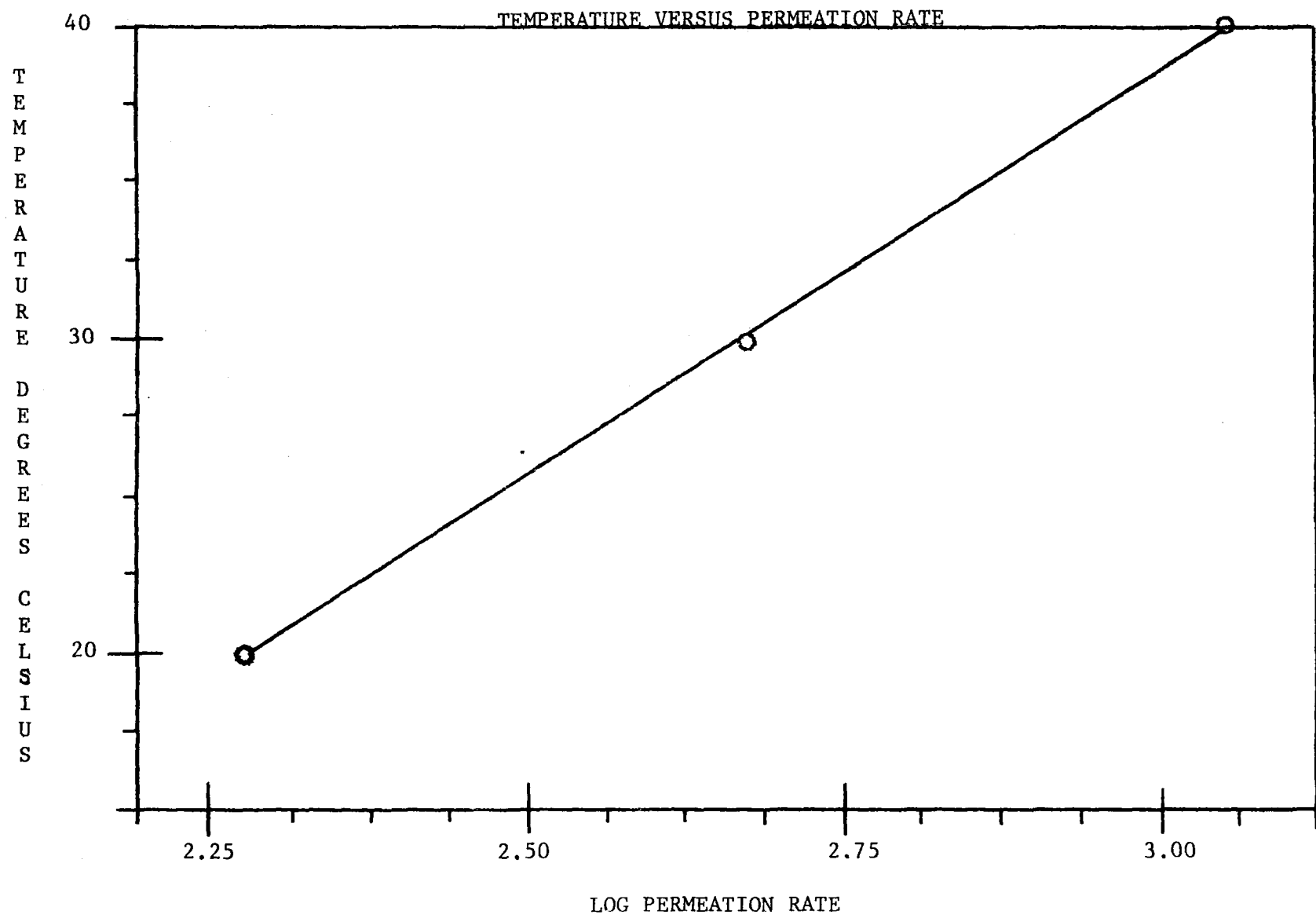


FIGURE 11

PLOT OF ABSORBANCE VERSUS HYDROGEN SULFIDE CONCENTRATION

ABSORBANCE VERSUS CONCENTRATION

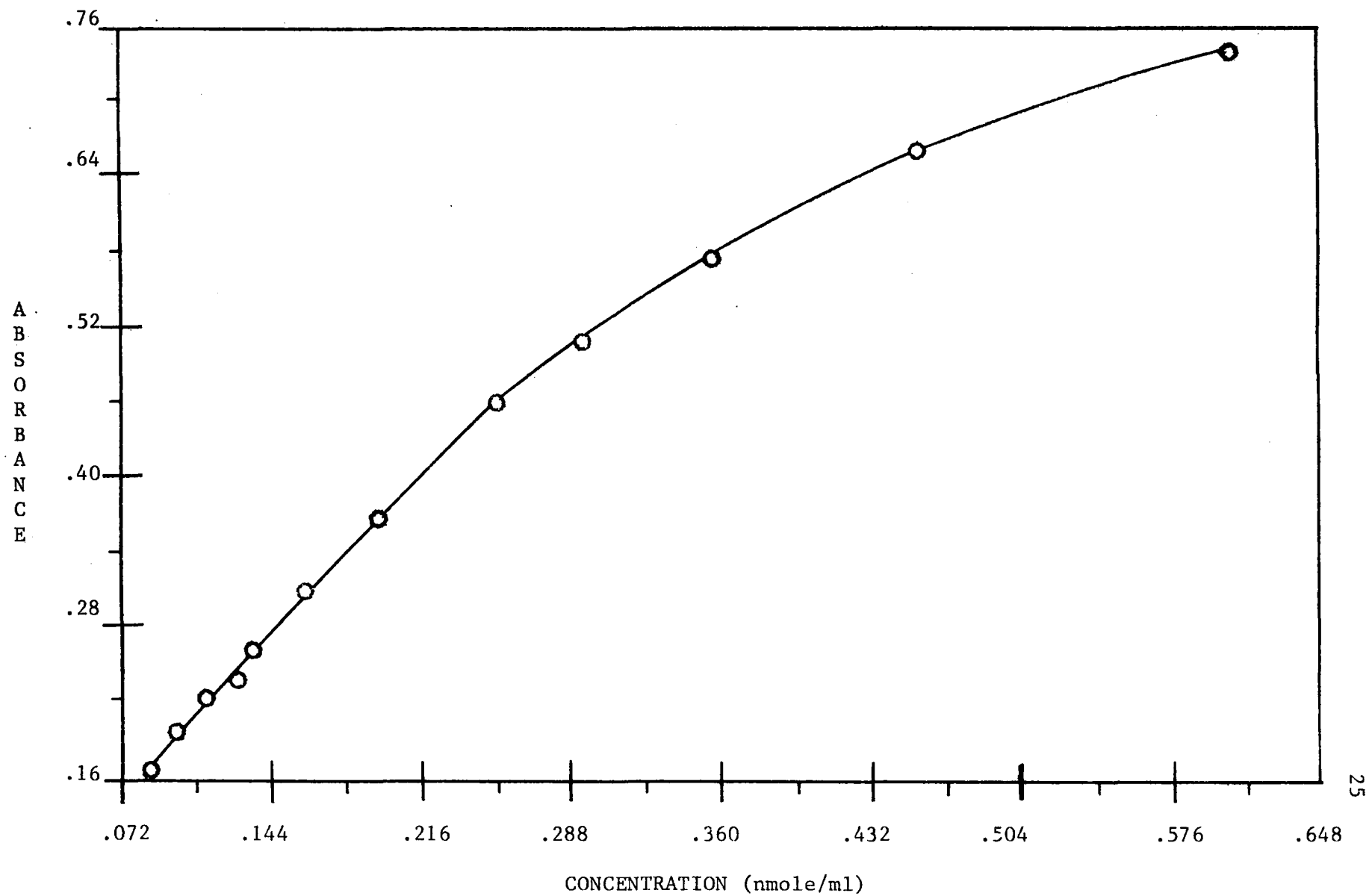


TABLE IV: (continued)

FLOW RATE (ml/min)	ABSORBANCE (a)	(H <sub>2</sub> S) (nmole/ml)
39	0.662	$4.56 \times 10^{-1}$
29	0.745	$6.09 \times 10^{-1}$

(a) Absorbance values given in the table are an average of two runs.

(b) The permeation tube was maintained at 25°C thus releasing 17.54 nmole/min of H<sub>2</sub>S, conversion temperature was maintained at 45°C.

#### Effects of Other Sulfur Containing Gases: Sulfur Dioxide

The possible interference of sulfur dioxide was investigated.

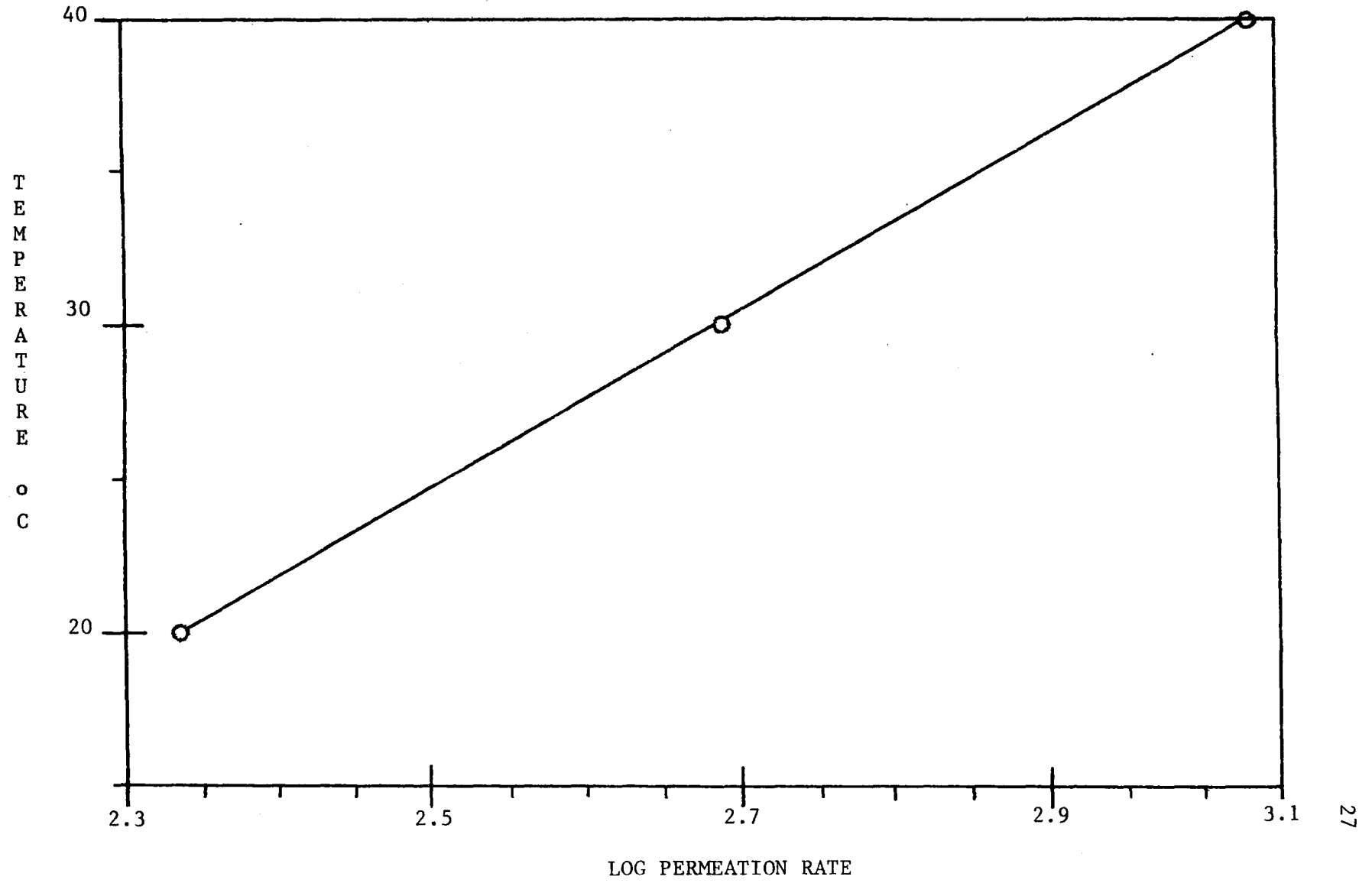
A permeation tube containing sulfur dioxide was inserted in the 'standard' position of the apparatus shown in Figure 1. The concentration of sulfur dioxide was permitted to buildup for fifteen minutes and then released over a five to eight second interval by drawing scrubbed air over the permeation tube and through the conversion tube. No response was observed other than usual background readings. In this test a ten centimeter sulfur dioxide permeation tube was used. Tube temperature was maintained at 23°C while the conversion temperature was held at 45°C. The permeation rate of the sulfur dioxide tube was determined from information given by the manufacturer and is shown in Figure 12. To ascertain that there was no response to sulfur dioxide we allowed both the concentration of hydrogen sulfide and of sulfur dioxide to buildup and then passed the accumulated gases over the conversion material. The response was noted. Several other tests were done using one or both of the permeation tubes. These data



FIGURE 12

PLOT OF TEMPERATURE VERSUS LOG PERMEATION RATE  
PER CENTIMETER OF TUBE LENGTH FOR SULFUR DIOXIDE

TEMPERATURE VERSUS LOG PERMEATION RATE



are shown in Table V.

TABLE V: INTERFERENCE STUDIES

GAS	BUILDUP TIME (MIN)	PERMEATION RATE	ABSORBANCE
SO <sub>2</sub>	15 min	86.00 nmole/min	0.041
H <sub>2</sub> S	15 min	14.73 nmole/min	0.377
SO <sub>2</sub> and H <sub>2</sub> S	15 min	100.73 nmole/min	0.398

(a) Rate given is total of permeation rates for both gases.

Effects of Other Sulfur Containing Gases:

Lower Alkyl Mercaptans

The possible interference of lower alkyl mercaptans was studied using methyl mercaptan as a sample. Conversion temperature was held at 45°C and the permeation tube at 24°C. After a twenty minute buildup time the methyl mercaptan was drawn over the conversion material as previously described. An absorbance signal of 0.854 was observed indicating the mercaptans would react with mercurous chloride to release mercury just as the hydrogen sulfide did. Data obtained in these studies are shown in Table VI. Permeation rates of the methyl mercaptan were determined from information given by the manufacturer and are shown in Figure 13.

FIGURE 13

PLOT OF TEMPERATURE VERSUS LOG PERMEATION RATE  
FOR A TEN CENTIMETER METHYL MERCAPTAN TUBE

TEMPERATURE VERSUS LOG PERMEATION RATE

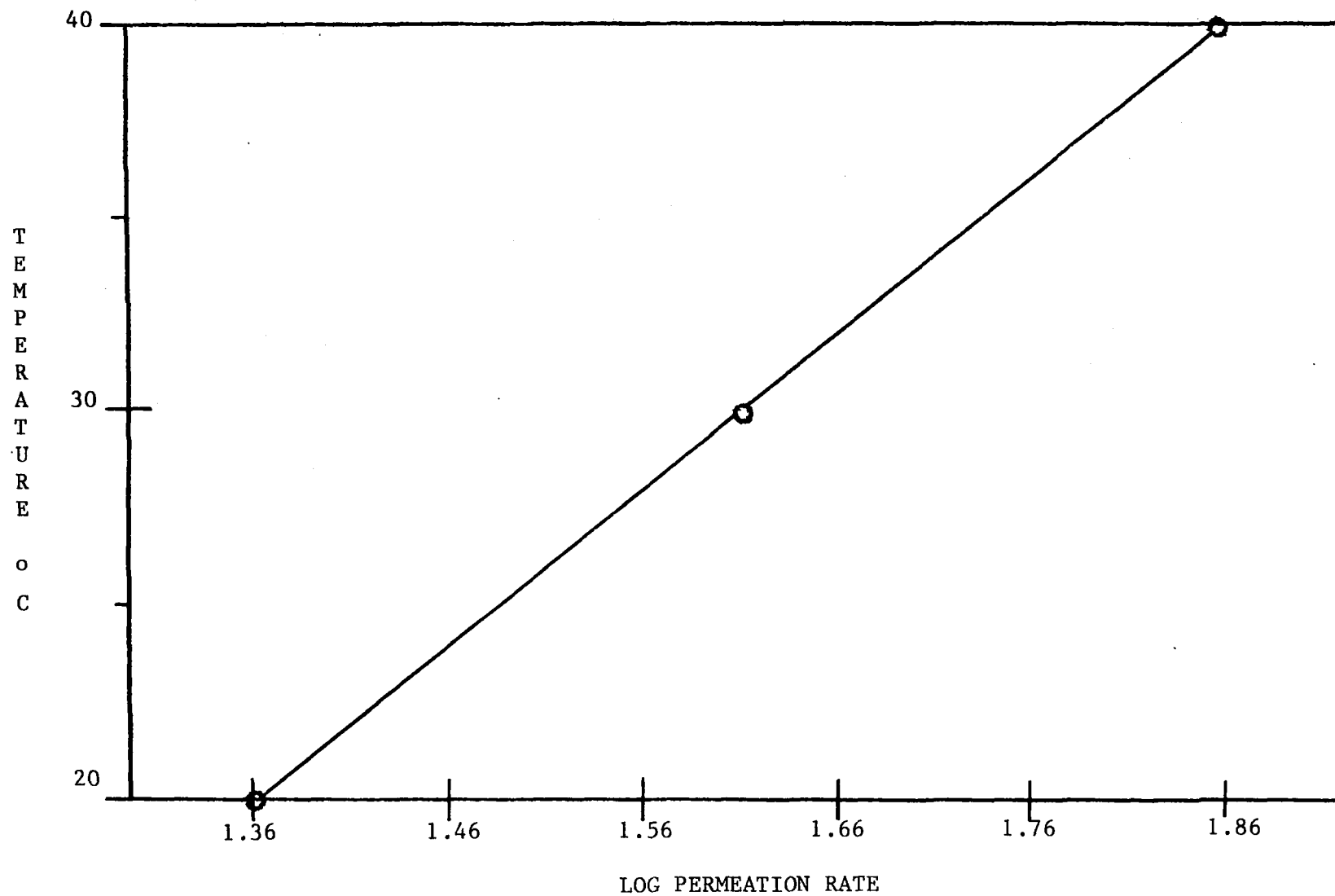


TABLE VI: INTERFERENCE STUDIES

GAS	BUILDUP TIME (MIN)	PERMEATION RATE	ABSORBANCE
CH <sub>3</sub> SH	20 min	6.05 nmole/min	0.854
H <sub>2</sub> S	15 min	16.08 nmole/min	1.000
CH <sub>3</sub> SH and H <sub>2</sub> S	16 min	22.13 nmole/min	1.222

(a) Rate given is total of permeation rates for both gases.

Response of Methyl Mercaptan  
as a Function of Concentration

Because of the findings of the above study it was necessary to determine whether the response to the mercaptan followed the Beer-Lambert law. Before any concentration study was done, the response to scrubbed air was measured as a function of the flow rate. The absorbance for the range from 200 ml/min to 10 ml/min only changed from 0.027 to 0.046 showing that the flow rate had little effect on the background. These data are shown in Table VII.

TABLE VII: FLOW STUDIES

FLOW RATE (ml/min)	ABSORBANCE
190	0.027
150	0.027
120	0.029
100	0.032
70	0.032
50	0.034
30	0.039
10	0.046

The concentration of mercaptan allowed to reach the conversion tube was controlled by varying the flow rate as previously done in the concentration study for hydrogen sulfide. A ten centimeter methyl mercaptan permeation tube was used and kept at 26°C. Conversion temperature was maintained at 45°C. The data shown in Table VIII is the average of two sets of data obtained in the above study.

TABLE VIII: CONCENTRATION STUDIES

ABSORBANCE	FLOW RATE (ml/min)	CONCENTRATION (nmole/ml)
0.097	200	$3.36 \times 10^{-2}$ (a)
0.106	190	$3.54 \times 10^{-2}$
0.111	180	$3.74 \times 10^{-2}$
0.120	170	$3.96 \times 10^{-2}$
0.137	160	$4.21 \times 10^{-2}$
0.155	150	$4.49 \times 10^{-2}$
0.173	140	$4.81 \times 10^{-2}$
0.188	130	$5.18 \times 10^{-2}$
0.208	120	$5.61 \times 10^{-2}$
0.231	110	$6.12 \times 10^{-2}$
0.260	100	$6.73 \times 10^{-2}$
0.288	90	$7.48 \times 10^{-2}$
0.319	80	$8.41 \times 10^{-2}$
0.382	70	$9.61 \times 10^{-2}$
0.423	60	$1.12 \times 10^{-1}$
0.475	50	$1.35 \times 10^{-1}$

TABLE VIII (continued)

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(a) Concentrations based upon a permeation rate of 6.73 nmole/min of methyl mercaptan

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The above data are shown in Figure 14.

#### Flow Dependence Studies

In order to test the spectrophotometer used for a flow dependence, both a ten centimeter hydrogen sulfide tube and a two centimeter tube were used at different flow rates. The ten centimeter tube was sampled at 200 ml/min, and the two centimeter tube sampled at 40 ml/min. The response observed was the same within experimental error.

#### Use of Silanized Glass Wool as a Solid Support for

##### Conversion Material

It was found that use of the Porasil solid support presented serious problems in response time. Response times for hydrogen sulfide at the 45°C conversion temperature were extremely long and could not be used for monitoring the gas in real time. Because of this the possibility of using glass wool coated with mercurous chloride was examined as had been done during preliminary studies leading to this investigation. It was found that by sprinkling fine mercurous chloride powder on DMCS treated glass wool and shaking off the excess, enough mercurous chloride remained on the glass wool to make an effective conversion material. The coated glass wool was packed in a glass tube whose dimensions were eight centimeters long by four millimeters inside diameter. It was found that the response to hydrogen sulfide using this conversion material was on the order of several minutes as

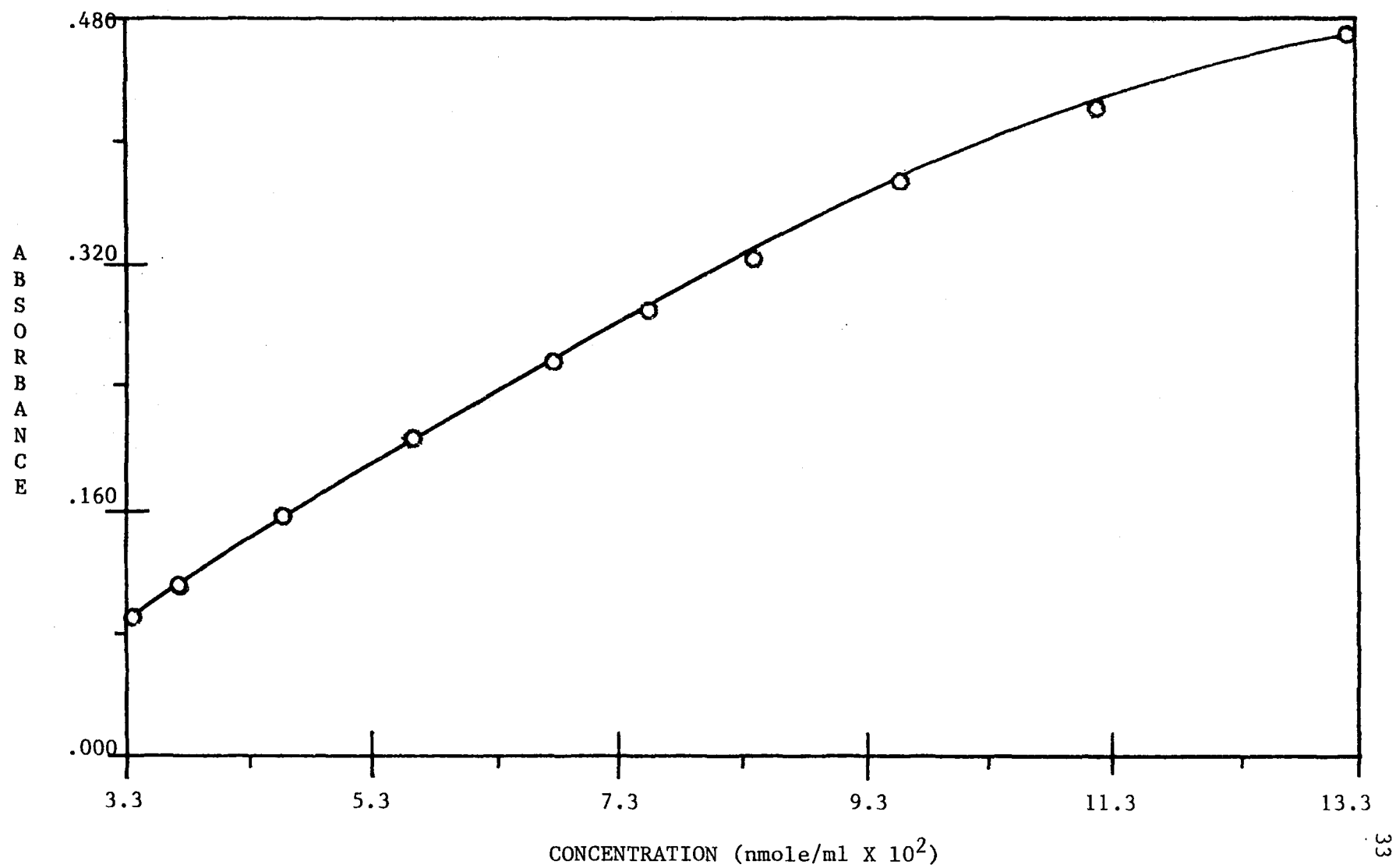


FIGURE 14

PLOT OF ABSORBANCE VERSUS METHYL MERCAPTAN CONCENTRATION

AT 45° C CONVERSION

ABSORBANCE VERSUS CONCENTRATION



compared to the excessive times encountered (up to thirty minutes) with coated Porasil beads. The conversion material made from the DMCS treated glass wool required no heating to obtain good response and was used at room temperature.

### Response of Hydrogen Sulfide as a Function of Concentration

#### Using a Glass Wool Conversion Support

The response of hydrogen sulfide as a function of concentration was studied. It was found that the two centimeter permeation tube released sufficient hydrogen sulfide to cause a full scale deflection while the low permeation wafer (permeation rate at 30°C is 30 nanograms/minute) only gave between 85 and 90% transmittance. Due to this it became necessary to set up a system to obtain various diluted concentrations of the gas evolved from the two centimeter tube. A 19.0 liter glass bottle was used for this purpose. The permeation tube was placed in the bottle and left in place continuously during the concentration study. Since both the permeation rate of the tube, and the volume of the jar were known, it was possible to calculate the concentration of hydrogen sulfide in the bottle at any given time. At selected time intervals samples were drawn from the system through the conversion tube. The conversion tube position was altered from near the glass apparatus to immediately before the mercury analyzer. The time intervals were chosen as the time necessary for the signal to drop to background levels. The concentration of the hydrogen sulfide present in the bottle at any given time was calculated from the following equation:

$$\frac{\text{Hydrogen Sulfide}}{\text{Concentration}} = \frac{\text{Pr} \cdot k \cdot t}{V} \text{ ppm}$$

where Pr is the permeation rate in nanograms per minute, k is the conversion factor to parts per million by volume and is equal to 0.719, t is the time the tube has been permeating in the bottle, and V is the volume of the bottle. For example with a 500 ng/min rate, four minutes of permeation time would give a concentration of hydrogen sulfide equal to 0.076 ppm.

Since drawing samples from the bottle effectively decreased the amount of available hydrogen sulfide, dilution effects were calculated from the sampling time and the flow rate of the instrument. The data were corrected for this effect. Data for several studies are shown in Table IX. Temperature during these studies was 23°C in one case and 24°C in the other case. It was found that at these temperatures the conversion efficiency was virtually the same from run to run, and conversion temperature was not controlled. The only effect of temperature in these studies was in the permeation rate of the hydrogen sulfide tube. This only affected the time required to reach a certain concentration of the gas. These data are given in Figure 15.

TABLE IX: CONCENTRATION STUDIES

H <sub>2</sub> S CONC. (ppb)	ABSORBANCE (a)	ABSORBANCE (b)
150		0.031
270		0.066
310	0.083	
410		0.091
530		0.108
560	0.122	

FIGURE 15

PLOT OF ABSORBANCE VERSUS HYDROGEN SULFIDE CONCENTRATION

● AT 23° C CONVERSION

▲ AT 24° C CONVERSION

TABLE IX (continued)

H <sub>2</sub> S CONC. (ppb)	ABSORBANCE (a)	ABSORBANCE (b)
640		0.125
740		0.136
860	0.152	
870		0.140
1020		0.149
1140	0.171	
1160		0.161
1250		0.167
1400	0.190	

(a) Absorbance signal observed for H<sub>2</sub>S permeating and converted at 24°C.

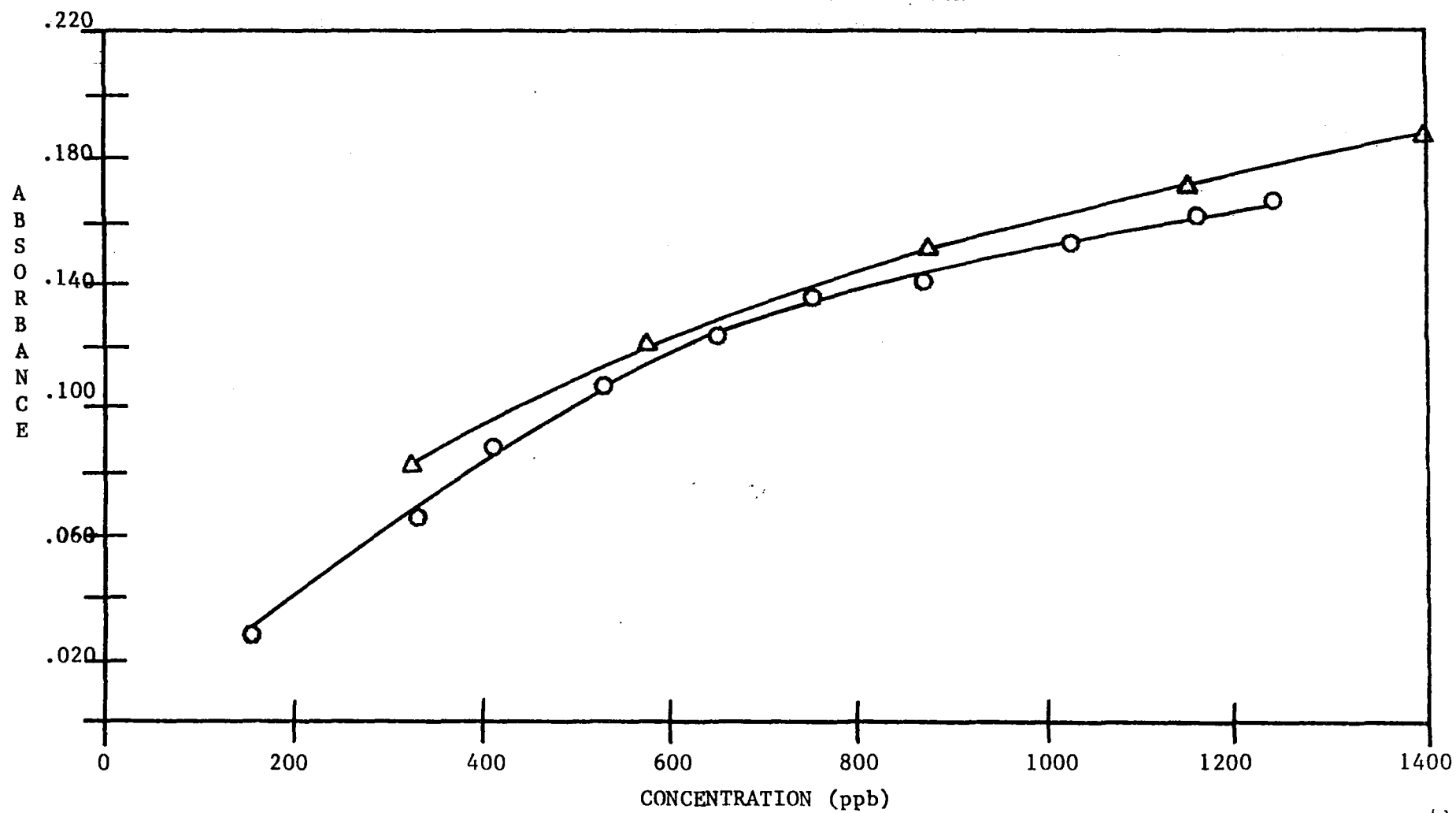
(b) Absorbance signal observed for H<sub>2</sub>S permeating and converted at 23°C.

During one of the concentration studies it was noticed that there were some pressure effects which led to a jump in the absorbance signal immediately after the hydrogen sulfide sampling was stopped. It was found that this was a result of too dense a packing in the conversion material. The problem was overcome by packing the conversion tube with less coated support. In this manner flow was maintained without a significant pressure drop.

#### Use of Magnesium Perchlorate as a Desiccant for the System

It was mentioned earlier that water is known to cause the decomposition of mercurous chloride; this could lead both to interferences in the determination of hydrogen sulfide, as well as to rapid

ABSORBANCE VERSUS CONCENTRATION



deterioration of the conversion material. Attempts at using magnesium perchlorate as a desiccant led to mixed results. When the desiccant was placed before the entrance of the air stream in the system of Figure 1, there was no variation within experimental error from the response obtained when the magnesium perchlorate was not used. The lack of any difference in the response signal when using a desiccant seems to indicate that the humidity in the laboratory air was not sufficient to cause a significant decomposition of the mercurous chloride on the solid support.

In later studies however the magnesium perchlorate was placed directly in the 19.0 liter bottle mentioned earlier. With this configuration absorption signals for increasing concentrations of hydrogen sulfide were significantly lower than when the desiccant was not used. This indicated that magnesium perchlorate does absorb hydrogen sulfide. The data obtained in the presence of magnesium perchlorate are given in Table X. Figure 16 shows the comparison between signals with or without magnesium perchlorate.

TABLE X: RESPONSE SIGNAL OF HYDROGEN SULFIDE  
IN THE PRESENCE OF MAGNESIUM PERCHLORATE

H <sub>2</sub> S CONCENTRATION (ppb)	ABSORBANCE
100	0.004
220	0.009
320	0.013
420	0.018
520	0.036
590	0.045
655	0.055
710	0.061



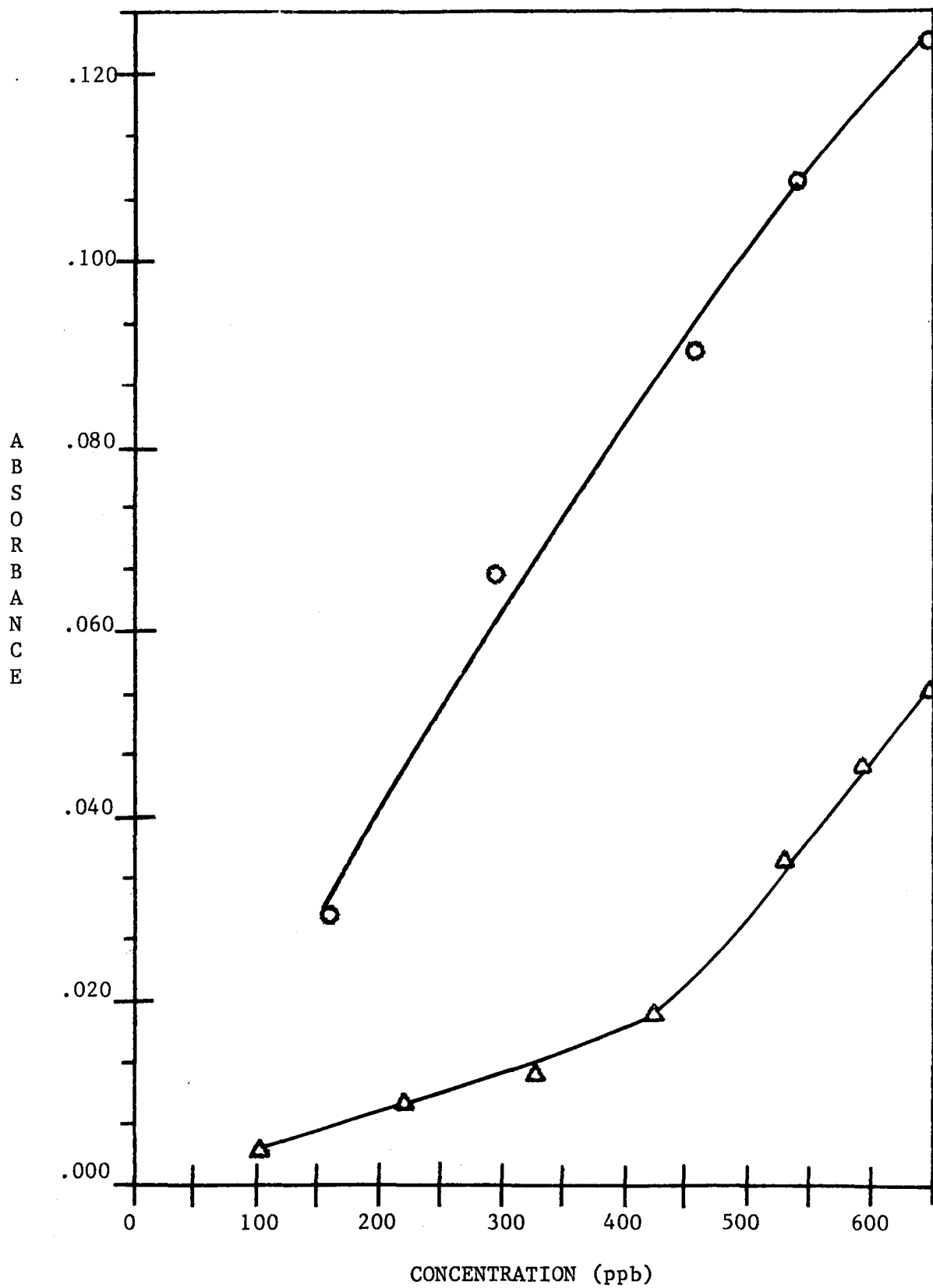
FIGURE 16

PLOT OF ABSORBANCE VERSUS HYDROGEN SULFIDE CONCENTRATION

Δ IN THE PRESENCE OF MAGNESIUM PERCHLORATE

○ IN THE ABSENCE OF MAGNESIUM PERCHLORATE

## ABSORBANCE VERSUS CONCENTRATION



### Determination of Hydrogen Sulfide in the Laboratory Environment

In order to verify the system and its operation, the air in the laboratory was sampled and analyzed for hydrogen sulfide. The low permeation wafer was used as a source of known concentrations of hydrogen sulfide. This device permeates at a rate of 30 ng/min at 30°C. The change in permeation rate of this device with temperature is directly proportional to the change of rate of the two centimeter tube. At 24°C the device releases 18 ng/min. At a flow rate of 200 ml/min and a conversion temperature of 24°C, the wafer gave an absorption signal of 0.039 units. When the air from the laboratory was sampled no response was observed other than background.

### CHAPTER III

#### DISCUSSION

Studies of the gas-solid reaction between hydrogen sulfide and mercury(I) chloride provide an insight into its use as a means for indirect, real time monitoring of hydrogen sulfide in the atmosphere. The study also provides insight towards the application of known solution reactions to their corresponding gas-solid reactions. Additional information about both hydrogen sulfide and mercurous chloride was also obtained.

The use of mercuric chloride as a scrubbing agent for air streams used in the calibration of the system confirms that the solution reactions mentioned earlier do proceed as gas-solid reactions. The reduction of mercuric chloride by elemental mercury which is usually performed by subliming a mixture of the two (9), was also shown to occur as a gas-solid reaction. It was imperative that our calibration system have a material that would effectively stop interfering substances which have been previously mentioned. A possible problem arises from the fact that any trapped mercury, by the nature of its reaction with the trap material, will produce mercurous chloride which could react with sulfur gases. The amount of mercury in the laboratory environment has been found not to be sufficient to cause a significant interference in these studies.

By studying the response to hydrogen sulfide as a function of temperature, an increase in the response with temperature was observed

(Figure 8). A change in rate of the reaction is indicated at approximately 45°C. This same change of rate was also observed in the study of the decomposition of mercurous chloride conversion material as a function of temperature. Subtracting the signal due to the decomposition of mercurous chloride from the response signal to hydrogen sulfide linearized the plot somewhat. From this information it is probable that the decomposition of mercurous chloride and not the reaction of hydrogen sulfide with the former is the cause of the change in rate observed at approximately 45°C.

With the use of Porasil C as a solid support for the mercurous chloride it was found that the response of the system was too slow to permit monitoring in real time. The rise, and more so the return time for the response signal was extremely long, thus suggesting surface adsorption of the evolved mercury onto the Porasil C beads. The use of silanized supports did not alleviate the problem. The relatively high background observed (0.086 absorbance units at 55°C) when using the Porasil C support at high temperatures, and the lack of any improvement in the response time with silanization of the beads suggest continued decomposition of the mercurous chloride. This behavior was especially noted when the conversion temperature was raised above 50°C. At these temperatures the decomposition of mercurous chloride became excessive. Since Duval (4) reported that mercurous chloride was stable up to 130°C in a dry atmosphere, it is believed that at high temperatures the amount of water vapor in the laboratory could be sufficient to enhance the decomposition of this salt, while at lower temperatures (24°C) it has a much less pronounced

effect. The stability of a thin layer of mercurous chloride could be substantially less than that of a larger mass. The stability of the mercurous chloride could be affected by factors changing the kinetics of the decomposition reaction. These include particle size as well as changes in heating rates.

When only the conversion of hydrogen sulfide to mercury is considered, it is found that the Beer-Lambert law is followed well for concentrations in the range of 1.8 to 15 ppm. The linearity of the data is excellent up to seven parts per million. Beyond that, as is commonly the case in absorption methods, the slope of the line decreases with increased concentration of the gas. The use of Porasil C beads as a solid support for the conversion of hydrogen sulfide to mercury is then recommended only for use as a grab sample method where the response time is not as critical as it is in real time monitoring.

During concentration studies the possibility of a flow dependence in the mercury analyzer was considered. It was assumed that the instrument was flow independent because the response signal for ten centimeter hydrogen sulfide tube sampled at 200 ml/minute the same as the response for a two centimeter tube sampled at 40 ml/minute. This shows that the ratio of hydrogen sulfide concentration to response holds constant (within experimental error) independent of flow rate. The good linearity of the Beer law plot when using the varying flow method to change the gas concentration indicates no flow dependence of the instrument, as flow dependence would result in distortion of the curve.

The use of DMCS treated glass wool as a solid support for mercurous chloride led to better response time as well as to better sensitivity. The absorption signal for parts per billion concentrations of hydrogen sulfide rises and levels off within several minutes; the return to background from maximum absorbance also occurs within several minutes. The time constant of an instrument is defined as the time required to reach  $1 - 1/e$  ( $e$  is the Napierian base and is equal to 2.718), or 63 per cent of the maximum absorption signal for a given concentration. Since in this experiment the time constant of the chart recorder used was less than one second, the time required to reach 63 per cent of maximum signal was considered to be the time constant of the monitoring system. It was found that by changing the position of the conversion tube from its position in Figure 1 to just before the mercury analyzer, the time constant of the system was decreased. This is probably due to the fact that the evolved mercury could flow more readily into the absorption cell without the chance of being adsorbed on the walls of the two to three foot section of Tygon tubing previously located after the conversion tube. When using DMCS treated glass wool as a support the time constant was found to lie between 45 and 50 seconds, depending upon the concentration of hydrogen sulfide present. A typical response signal to hydrogen sulfide is given in Figure 17.

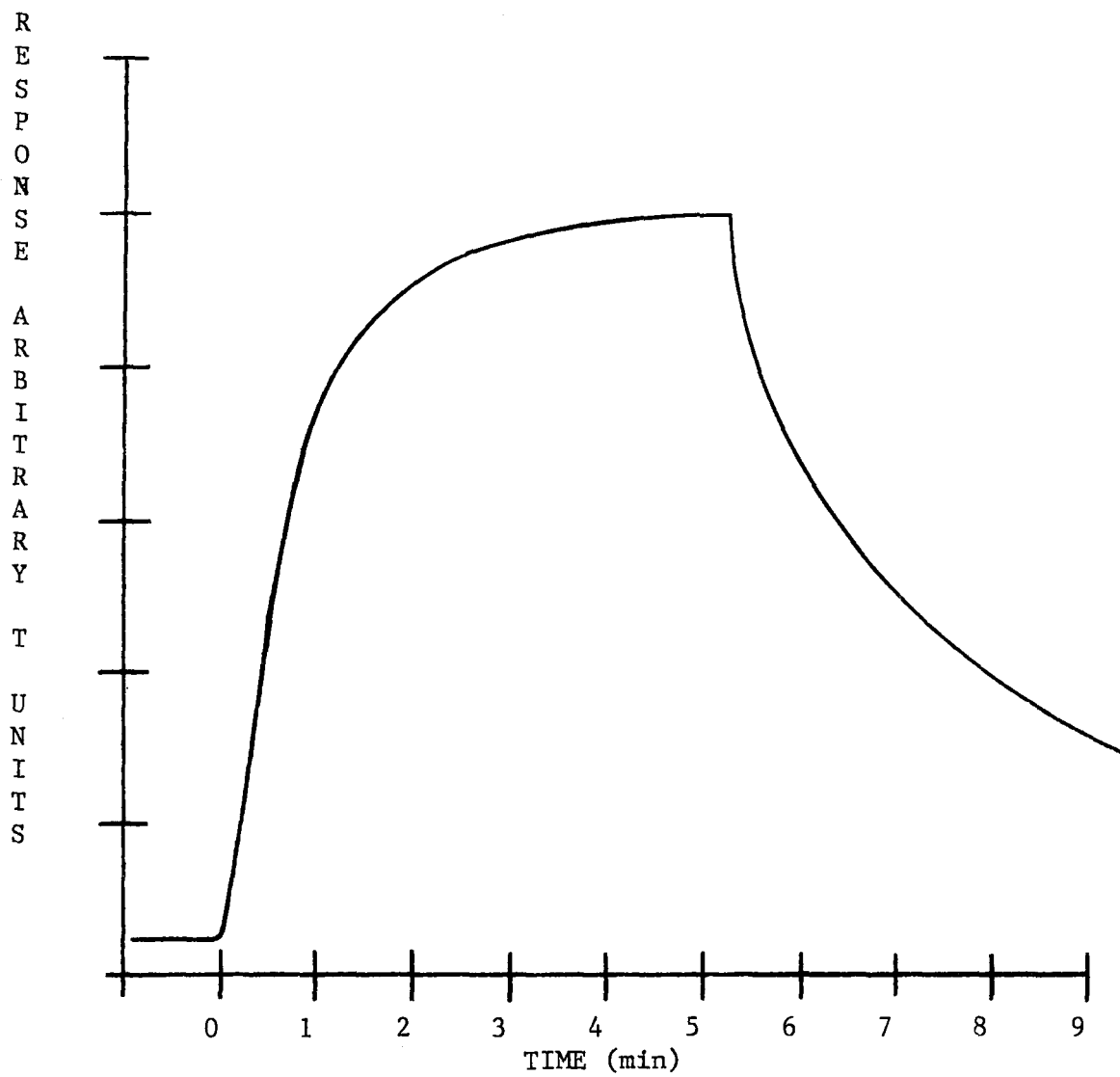
The concentration range that can be measured using silanized glass wool as a support is one order of magnitude lower than that observed when using Porasil C. We note adequate response to measure 150 ppb of hydrogen sulfide. However the linearity obtained with Porasil C

FIGURE 17

RESPONSE CURVE OBSERVED FOR HYDROGEN SULFIDE AT ROOM TEMPERATURE

CONVERSION ON DMCS TREATED GLASS WOOL





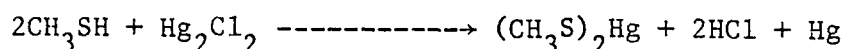
desorption of the evolved mercury could be enhanced by the larger mercaptan molecule covering a larger area than the hydrogen sulfide and thus leaving less available room for evolved mercury to remain adsorbed on the support. It must also be noted that not all the hydrogen sulfide entering the conversion tube is converted to measurable mercury in the elemental state since a certain amount is undoubtedly adsorbed on the support and walls of the tubing.

The effect of desiccation using magnesium perchlorate on the system was studied. It was found that when magnesium perchlorate is left in contact with the hydrogen sulfide, the absorption signal is greatly reduced (Figure 16). This indicated that magnesium perchlorate absorbs hydrogen sulfide in a manner similar perhaps to its absorption of water. Since sulfur is the higher homologue of oxygen the two molecules are very similar and absorption of the hydrogen sulfide by the magnesium perchlorate is not surprising. Using a desiccant at the entrance of the air stream into the calibration system did not have a noticeable effect in the laboratory at low conversion temperatures. At high conversion temperatures, where decomposition of mercurous chloride might already be pronounced, the use of a drying agent is necessary. However the use of high conversion temperatures is not recommended. For measurements made in the field where the humidity may be high, further decomposition of the mercurous chloride could occur. However magnesium perchlorate should not be the choice of desiccant as it would absorb any hydrogen sulfide to be measured. Another desiccant that would not absorb hydrogen sulfide needs to be found.

is better than that observed with the use of glass wool. Linearity with the glass wool is maintained up to 600 ppb, from 600 ppb to 1.4 ppm the plot curves towards the concentration axis. Since the glass wool support is used at ambient room temperatures, the high background levels (0.013 with glass wool at 23°C as compared to 0.086 at 55°C on Porasil C) due to the decomposition of the mercurous chloride at elevated temperatures were avoided. At the low conversion temperatures used there was a slight rise in the conversion efficiency with temperature. This is readily seen by comparing the absorbance values for concentration studies done at 23°C and 24°C (Table IX, Figure 15).

From the study of effects of other sulfur containing gases, it was found that large concentrations of sulfur dioxide did not interfere with the hydrogen sulfide to mercury conversion. No change in the absorption signal for hydrogen sulfide was observed in the presence of sulfur dioxide at six times the concentration of the former.

The study of effects of lower alkyl mercaptans shows that methyl mercaptan, and hence other mercaptans, would actively interfere with the hydrogen sulfide to mercury conversion. Concentrations of methyl mercaptan showed an absorption signal equivalent to that observed with twice the concentration of hydrogen sulfide. The cause of this large response is not clear, as the following reaction had been proposed as possibly occurring.



Here it is possible that a better release of the evolved mercury could occur than with the hydrogen sulfide due to the larger mercaptan molecule covering more surface area. This comes from the fact that

With the present system concentrations as low as 15 ppb could be measured. Since OSHA limits for industrial exposure are set at a maximum of 20 ppm over an eight hour interval, the current experimental setup could not be used as is for monitoring at these levels. As the measuring system is based upon atomic absorption, the absorbance is directly proportional to both the concentration of absorbing species, and the path length of the monochromatic beam through the sample. In order to vary the range of concentrations that could be measured, the path length could be altered. If the cell length were decreased by an order of magnitude, the concentrations measureable would be increased by an order of magnitude. Thus by use of a variable cell length this system could be set up to monitor hydrogen sulfide at levels about the OSHA standards, while still maintaining the ability to monitor sub parts per million concentrations of the gas.

The system could further be improved by the use of double beam optics in the spectrophotometer. This would especially be useful at higher conversion temperatures where the mercurous chloride decomposition caused an increase in the absorption signal. Since the signal due to decomposition of the mercurous chloride would be seen by both the reference and measuring beams, it could be subtracted from the signal due to the hydrogen sulfide (or mercaptan), and only the net signal would be recorded.

In the study of the hydrogen sulfide present in the laboratory environment a low permeation wafer was used as a source of a low concentration of hydrogen sulfide. From the manufacturers information the permeation rate at 24°C was determined to be 18 ng/min. At a flow

rate of 200 ml/min this corresponded to a concentration of 65 ppb. The absorbance signal for this concentration was found to be 0.039. Using this as a calibration standard the laboratory air was analyzed and the hydrogen sulfide concentration present was found not sufficient to be detected by the system. This is not surprising as ambient concentrations of hydrogen sulfide are usually in the low parts per billion or less range.

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