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# Development of Analytical Reference Materials and Contaminant Generation Systems - Work Completed During Fiscal Year 1973

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National Bureau of Standards  
Department of Commerce  
Washington, D. C. 20234

January 1973

Interim Report

Prepared for  
National Institute for Occupational Safety and Health  
Division of Laboratories and Criteria Development  
Cincinnati, Ohio 45202



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**DEVELOPMENT OF ANALYTICAL REFERENCE  
MATERIALS AND CONTAMINANT GENERATION  
SYSTEMS – WORK COMPLETED DURING  
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**U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary**  
**NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director**



DEVELOPMENT OF ANALYTICAL REFERENCE  
MATERIALS AND CONTAMINANT GENERATION SYSTEMS -  
WORK COMPLETED DURING FISCAL YEAR 1973

ABSTRACT

This report summarizes the research and development activities performed by NBS for NIOSH, during Fiscal Year 1973, under Interagency Agreement 123/3104459. Items reviewed included: reference materials consisting of filters containing hazardous metals and quartz-clay mixtures; analytical standards for determination of organic solvents; the development of air contaminant generator systems; reference samples consisting of blood and urine with analyzed amounts of toxic elements.

INTRODUCTION

Work was completed or substantial progress was made on all items identified in the Memorandum of Agreement. The activities carried out during Fiscal Year 1973 are outlined in the following sections, identified to correspond to the tasks described in the Memorandum of Agreement and reference is given to NBS reports for full details on the tasks completed. The progress on the remaining tasks is described in appendices A through D.

A. Atmospheric Analysis Reference Materials

Techniques were developed for the preparation and certification analysis of filters containing the following hazardous materials:

Series 1	Pb	Cd	Zn	Sn
	µg/filter			
1-A	7.5	5	100	150
1-B	15	10	200	300
1-C	30	20	400	600

Series 2	Pb	Zn	Mn
		µg/filter	
2-A	7.5	100	250
2-B	15	200	500
2-C	30	400	1000
Series 3	Be		
		µg/filter	
3-A	0.1		
3-B	0.2		
3-C	0.4		

One hundred sets of each series have been prepared, analyzed, and delivered to NIOSH for their evaluation and use. Full details are given in NBS Report NBSIR 73-256.

Techniques were developed for the preparation and certification analysis of filters on which mixtures of quartz and clay were deposited.

<u>Series</u>	<u>SiO<sub>2</sub>, µg</u>	<u>Clay, mg</u>	<u>Total, mg</u>
000100-160	0	400	400
000200-260	30	370	400
000300-360	80	320	400
000400-460	200	200	400

Fifty filters of each series were prepared, analyzed and delivered to NIOSH for evaluation and use as analytical standards. Full details are given in NBS Report NBSIR 73-400.

In each of the above cases, levels given are nominal values. The reports give the recommended analytical values.

#### B. Analytical Standards for Biological Materials

Work on blood samples containing biologically incorporated lead was completed and analyzed samples were delivered to NIOSH. The two sets of samples contained lead at "normal" and "elevated" levels, respectively.

Work was completed on the development and analysis of urine samples containing biologically incorporated mercury at "normal" and "elevated" levels. A total of 200 samples were delivered to NIOSH.

Techniques were developed and a number of freeze-dried samples of normal urine and urine spiked with elevated levels of selenium, arsenic, copper, nickel, and chromium were prepared and certified. A similar set of two samples containing "normal" and "elevated" levels of fluoride was also prepared and certified. These samples have been packaged in analytical units and delivered to NIOSH.

NBS Report 73-406 gives full technical details of the preparation and analysis of all of the biological samples mentioned above.

#### C. Mercury Vapor in the Industrial Environment

Work was done on the development of techniques for production and certification analysis of reference materials for the determination of mercury vapor in the occupational environ-

ment. A gas delivery system was constructed and performance evaluated. A lot of prototype tubes containing mercury deposited on iodized charcoal was prepared for method evaluation. Discussions shortly thereafter with the Project Officer indicated alternate other approaches to collection of mercury vapor were being considered. Accordingly, further production of charcoal tubes was suspended, awaiting NIOSH's clarification of the analytical technique.

The system for use in preparing the reference tubes is essentially that described in NBS Report NBSIR 73-254. The silver wool sampling technique appears to be very satisfactory for analytical purposes, but may not be feasible for routine use, due to cost considerations. Charcoal is superior as a collector, but there are analytical problems due to desorbition difficulties. A procedure in which charcoal is used for collection, followed by desorbition onto silver in the analytical step seems to be a satisfactory one.

D. Analytical Standards for Determination of Organic Solvents

See Appendix A.

E. Development of Generation Systems for Certification of Gas and Vapor Sampling Instruments

Gas generation systems were developed, constructed, and performance evaluated and reports have been prepared as indicated below. The modular concept was followed so that the systems developed and delivered vary from complete independent units, to gaseous mixtures for use with units already delivered.

Operational manuals have been prepared for each system. The pertinent NBS reports are as follows:

- NBSIR 73-254 - A Mercury Vapor Generation and Dilution System - E. P. Scheide, R. Alvarez, B. Greifer, E. E. Hughes, and J. K. Taylor
- NBSIR 73-255 - System for Preparation of Known Concentrations of Methane in Air - E. E. Hughes, W. D. Dorko, and J. K. Taylor
- NBSIR 73-257 - Ion Selective Electrodes for Industrial Hygiene Monitoring: Hydrogen Cyanide - E. P. Scheide, E. E. Hughes and J. K. Taylor
- NBSIR 73-258 - A Gas Dilution System for Acrolein - E. P. Scheide, E. E. Hughes and J. K. Taylor
- NBSIR 73-259 - A Gas Dilution System for Methyl Bromide - E. P. Scheide, E. E. Hughes and J. K. Taylor
- NBSIR 73-260 - A Gas Dilution System for Arsine-Air Mixtures - P. A. Pella, E. E. Hughes and J. K. Taylor
- NBSIR 73-261 - A Gas Dilution for Hydrogen Fluoride-Air Mixtures - P. A. Pella, E. E. Hughes and J. K. Taylor
- NBSIR 73-292 - Gas Generating Systems for the Evaluation of Gas Detecting Devices - E. E. Hughes, W. D. Dorko and J. K. Taylor

In addition to the systems developed, considerable effort was devoted to three additional systems. This work is summarized in attachments to this report, as indicated below:

Sulfuric Acid Aerosol, see Appendix B

Phosgene, see Appendix C

TDI and MDI, see Appendix D

Formaldehyde, see Appendix E



APPENDIX A

Progress Report

on

Development of Charcoal Tubes  
as SRM's for Organic Vapor Analysis

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## 1. INTRODUCTION

This is the second progress report on the preparation of charcoal tubes containing known amounts of organic solvents. The first report, issued December 1, 1972, dealt with the preparation of an initial batch of approximately 1,000 tubes, each containing known amounts of one of seven solvents, viz., benzene, xylene, dioxane, chloroform, carbon tetrachloride, ethylene dichloride, and trichloroethylene. Together, the two reports contain descriptions of work done during FY 1973.

This report describes results obtained since December 1972 and includes plans for future work.

## 2. RE-EXAMINATION OF REPORTED VALUES FOR CHARCOAL TUBES

In the first report, values for the amount of adsorbed solvent were given for each charcoal tube. These were calculated values from a computer-fitted straight line through data points obtained from the analysis of the tubes and from the flow-rates and concentrations of the gases used to prepare the tubes. The predicted values, based on the gas concentrations-flow data, formed the X-axis, while the analyzed values for the tubes formed the Y-axis. The reported results were based on the fitted line through the points determined by the predicted and analyzed values; this procedure gives greater weight to the values based on the gas concentration.

Re-examination of the methods used to prepare the gas mixtures has shown that errors may have been introduced in the

dilution steps. (This is discussed in detail in Section 4 of this Appendix.) A few of the retained charcoal tubes containing benzene have been analyzed recently, and the results from this analysis are significantly different from the values reported earlier -- in fact, these new data place the values for benzene closer to the values reported by the participating laboratories. To further clarify this situation, a number of tubes have been re-analyzed and new values will be assigned. (A separate report giving full details will be issued.)

However, even though the final values for the tubes may be amended, the tubes themselves show little variability in the quantity of adsorbed material. Thus, the tubes of a particular concentration level, those labeled "E", for example, show a range of variation less than 2 percent. This is true, too, for the tubes labeled A, B, C, and D. Similarly, the ratio of the adsorbed material of any two tubes is essentially equal to the ratio of the flow rates of the sampling orifices to which they were attached during the filling operation. Accordingly, their homogeneity does not appear to be in doubt. Therefore, regardless of the absolute value of the contents contained in the tubes, any variation in the analysis of the tubes at a given level that is greater than a few percent would indicate variability in the analytical procedure.

The work to be performed for the Standard Reference Material Charcoal Tubes (SRM's) will not, of course, depend solely on analysis of the tubes, but will also be based on

the analysis of the gases used to fill the tubes. This will be discussed in the following sections of this report.

### 3. DEVELOPMENT OF SAMPLING SYSTEM AND EXPERIMENTAL DESIGN FOR THE PREPARATION OF CHARCOAL TUBE SRM'S

For the preparation of the original 1000 charcoal tubes, a sampling system was used which provided constant flow at each of five orifices -- but not identical flow. In fact, the range of flow varied by about 10 percent. Thus, five different values were listed for the charcoal tubes at each nominal concentration level. For the SRM's, it was decided to prepare tubes that can be certified to contain the same amount of solvent, at each concentration level, within a certain known error.

Since 4200 tubes are required to be filled for the SRM's it was necessary to redesign the sampling manifold and to develop a procedure which would provide matched orifices in sufficient number to insure that the tubes could be filled in a reasonable length of time. It was felt that a sampling manifold containing about two dozen matched orifices would be suitable.

The final design has provision for 20 critical orifices. The orifices are mounted on a hollow brass base plate, 16.5 cm (6.5 in.) in diameter and 1.9 cm (0.75 in.) in height. Each critical orifice is a hypodermic needle (22 gauge) selected so that the range of flow through all orifices varies by no more than 1.5 percent. The selection of the needles necessitated

the testing of about 200 needles for flow characteristics. The needles are fitted into Luer-loks<sup>1</sup> (obtained from hypodermic syringes) and were made vacuum-tight with the aid of stopcock grease. The Luer-loks are soldered into the baseplate. This arrangement makes it possible to remove or replace needles when necessary.

Atop the needles are placed Nupro<sup>1</sup> filters to protect the needles from contamination by particulates. The tubes are attached by short pieces of rubber tubing to the apparatus. In use, the baseplate is connected to a vacuum source.

For the filling of the tubes at concentrations corresponding to 0.5, 1.0 and 2.5 times the OSHA level, a single gas mixture will be employed. The use of a single gas mixture should simplify the analysis of the gas and more importantly, should produce tubes that have a definite known relationship to each other. The tubes, for example, at the 1.0 OSHA level will contain twice as much solvent vapor as the tubes at the 0.5 OSHA level. The amount collected will be determined by the length of sampling time. These tubes will contain a quantity of solvent equal to that which would have been adsorbed if a sample were collected at the rate of one liter per minute for

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<sup>1</sup>Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the NBS, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

ten minutes in an atmosphere containing solvent vapor at a concentration of 0.5, 1.0, and 2.5 times the OSHA level.

Thus, for the sampling orifices described above, which have flow rates of about one liter per minute, the sampling time needed to collect a sample equivalent to 2.5 times the OSHA level would be ten minutes, if the gas concentration is 2.5 times the OSHA level. Similarly for tubes at the 0.5 and 1.0 levels, the sampling times would be two minutes and four minutes.

#### 4. DEVELOPMENT OF METHODOLOGY AND CRITERIA FOR PREPARATION AND ANALYSIS OF SOLVENT-IN-AIR MIXTURES

As pointed out earlier, the re-examination of the pressurized tank mixtures of solvents-in-air has shown that errors in the determination of the solvent concentrations may have been introduced. This could occur when the assumption is made that a dilution of a primary tank mixture to produce a second tank mixture will yield a concentration of solvent vapor which is directly proportional to the dilution factor. Recent analyses have shown that this error can be as large as 7 percent when, for example, trichloroethylene at 1000 ppm is diluted to 100 ppm. Accordingly, additional work on solvents-in-air has been devoted to problems inherent in preparing and analyzing these mixtures.

In the preparation of these mixtures, the solvent is introduced into evacuated size 1-A tanks either by distilling the solvent or by injecting the solvent into the tank. The tank is then pressurized to about 1000 psia. The concentration

may be calculated from (1) the weight of the solvent admitted, the total volume of the tank and the final pressure; or (2) the pressure of the solvent vapor and the final pressure.

In fact, measurements agree with calculated values within about 2 percent when solvent-in-air mixtures in the range of 200-1000 ppm are prepared. The problem, then, occurs upon dilution of these tank mixtures to levels near the OSHA range.

The dilution step, say from 600 ppm to 60 ppm is achieved by withdrawing 10 percent of the original tank mixture and transferring it to a second tank of the same size. This second tank is then diluted with air to a final pressure of 10 times the pressure of the transferred gas. It is at this step that anomalies present themselves -- i.e., the discrepancy between concentration based on pressure - dilution data and concentration based on gas chromatographic data. This can be seen by comparing the figures given below, in which gas dilution data are compared with gas chromatographic data

<u>Solvent</u>	PPM Gas <u>Calculated</u>	PPM G.C. <u>Method</u>	Percent Difference $\frac{\text{G.C.} - \text{Gas}}{\text{Gas}} \times 100$
Benzene	202 31.7	202 28.8	0 - 9.1%
Ethylene Dichloride	713 71.6	713 66.9	0 - 6.6%
Trichloro- ethylene	1016 98.1	1016 90.9	0 - 7.3%
Chloroform	728 73.5	728 65.3	0 -11%

Gas chromatographic analysis of gases is performed by transferring gas at known pressure and volume into the gas chromatograph equipped with a flame ionization detector. Response of the gas chromatograph measured in terms of area of the resulting peak, is directly proportional to the amount of compound contained in the sample. Therefore, a gas sample which is one-tenth as concentrated as a second gas sample should give a gas chromatographic response which is one-tenth as large as the second sample. This response is shown to be the case, for example, in tank mixtures of propane and methane. Similarly, liquid solutions of each of the seven solvents of interest (benzene, xylene, dioxane, chloroform, carbon tetrachloride, ethylene dichloride, and trichloroethylene) give linear gas chromatographic responses vs. concentration. However, in the gas mixtures of the seven solvents there are significant differences between calculated concentrations and concentrations obtained by gas chromatography. Although it may be assumed, perhaps quite generally, that the gas chromatographic data is correct, a confirmatory procedure is required to prove this.

One procedure which can be used to calibrate the gas chromatograph and thus determine the concentration of a solvent vapor would involve the following steps: replumbing of the gas chromatograph to enable alternate injection of liquid or gaseous samples; determination, to within 1 or 2 percent, of the volume of the gas sampling valve; accurately prepared liquid solutions of the desired solvent in a material such as

carbon disulfide; calibration of the gas chromatograph using the liquid standards; and finally the determination of the concentration of a gas mixture by comparing the gas response to a calibration curve for the liquid solution of the solvent.

A direct method for measurement of solvent concentration, which is now being used, involves collecting and weighing the solvent contained in a known volume of the solvent-in-air mixture. In this method, a calibrated orifice is used to obtain a constant collection rate, the sampling time is carefully controlled, and a trapping medium -- a charcoal tube -- is carefully weighed before and after the sampling. The concentration can then be easily calculated.

In this procedure the charcoal tube is connected to a sampling orifice and pure air is drawn through until the tube registers a constant weight. The solvent-in-air mixture is then drawn through the tube for a certain length of time. The weight gain of the tube and the flow through the tube are used to calculate the concentration of the gas mixture. The collection is quantitative for reasonable flow rates and the tubes have ample capacity to provide reliable measurements. For example, a tank mixture of carbon tetrachloride prepared at a concentration of 680 ppm, yielded results of 688 and 683 ppm by the charcoal tube method. Full details of this analytical method will be described in a future report.

## 5. PRESENT STATUS OF SRM PRODUCTION

The technical details of the procedure to produce the SRM tubes have now been developed to the point where production could be started. The tubes to be filled have been received and the gas mixtures have been prepared and analyzed.

The production of the SRM's is being held temporarily in abeyance, pending the NIOSH evaluation of the charcoal tube analytical procedure. Once final approval has been received, the work can be completed within a three-month period.



APPENDIX B

Progress Report

on

The Generation of Known Concentrations  
of Sulfuric Acid Aerosol

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## 1. INTRODUCTION

This report describes some preliminary results obtained in the generation of known concentrations of sulfuric acid aerosol. To gain some familiarity with producing such aerosols, a generating system was constructed which involved passing air at a known flow rate through concentrated  $\text{H}_2\text{SO}_4$  - fuming  $\text{H}_2\text{SO}_4$  mixtures. The entrained  $\text{SO}_3$  vapor was mixed with humid air in a mixing chamber and then allowed to pass through a sample manifold. To monitor the concentration of  $\text{H}_2\text{SO}_4$  aerosol in the sampling manifold, one port of the sampling manifold was fitted with a millipore filter assembly and connected to a mechanical pump. Qualitative determinations of the collected  $\text{H}_2\text{SO}_4$  aerosol on the millipore filter were made with  $\text{BaCl}_2$ . An alternate procedure for generating  $\text{H}_2\text{SO}_4$  aerosols was investigated which obviates the need for acid mixtures.

## 2. PREPARATION OF $\text{H}_2\text{SO}_4$ AEROSOLS FROM ACID MIXTURES

Historically, mixtures of concentrated - fuming  $\text{H}_2\text{SO}_4$  acids have been used to prepare aerosols in the tenth micron range (1,2). The use of known amounts of fuming  $\text{H}_2\text{SO}_4$  (i.e. oleum) will produce known  $\text{SO}_3$  concentrations above the solution as calculated from vapor pressure vs. temperature data. This procedure has also been used to prepare  $\text{H}_2\text{SO}_4$  aerosol particles for controlled growth studies using light-scattering techniques (2). Therefore, this method of preparation served as a starting point in the present study. Mixtures of the acids were prepared by adding known volumes of 30 percent fuming  $\text{H}_2\text{SO}_4$  (i.e. containing

30-33 percent free  $\text{SO}_3$ ) to the concentrated (96 percent by weight) acid. Solutions were prepared having  $\text{SO}_3$  partial vapor pressures from 1 to 10 mm Hg at 25°C. Such solutions would theoretically produce concentrations of  $\text{H}_2\text{SO}_4$  aerosols in the range from 1,300 to 13,000 ppm.

### 3. DESCRIPTION OF THE GENERATING SYSTEM

Figure 1 is a diagram illustrating the principle of operation. Air is first dried and then passed through two bubblers containing a mixture of the fuming and concentrated acids. The flow is controlled by means of a differential flow rate controller DFC-1 and measured with a rotameter. The air saturated with  $\text{SO}_3$  enters the mixing manifold and mixes with another stream of humid air. The air is humidified by passing it through a bubbler containing water. The flow is controlled by means of DFC-2 and measured with a rotameter. The humid air mixes with the  $\text{SO}_3$  stream to form the  $\text{H}_2\text{SO}_4$  aerosol. The aerosol passes to the sample manifold where a sample is collected via a millipore filter assembly for subsequent analysis. The presence of  $\text{H}_2\text{SO}_4$  collected on the filter was confirmed qualitatively with  $\text{BaCl}_2$ .

### 4. COMMENTS ON THE ACID MIXTURE METHOD OF PREPARING AEROSOLS

One of the major difficulties encountered in the above procedure is the method of preparing the sulfur trioxide. The preparation of hazardous acid mixtures on a routine basis would seem to be undesirable in a calibration system of this type. For this reason an alternate route was explored which if successful would obviate the need for such acid mixtures. The

contact process for the manufacture of  $H_2SO_4$  depends on the conversion of  $SO_2$  to  $SO_3$  catalytically. The advantages of using a catalytic conversion method here would be twofold. First a working standard could be prepared which would consist of a known concentration of  $SO_2$  in air or an  $SO_2$  permeation tube. The  $SO_2$  could be then converted catalytically to  $SO_3$  and mixed with humid air to produce a known concentration of the aerosol. Secondly, if the conversion efficiency was 100 percent or could be determined at each desired concentration level then the aerosol concentration may not require monitoring in contrast to the acid mixture method of preparation. For these reasons, some initial studies were undertaken to gain more information about this method.

##### 5. PREPARATION OF CATALYTIC CONVERTER

A catalytic converter was constructed and consisted of finely dispersed Pt metal (5-10 percent) on asbestos fibers. The fibers were loosely packed in a 12 in. long by 3/8 in. O.D. stainless steel tube as shown in Figure 2. The tube was placed in a furnace as shown and held at 350-450 °C for catalytic conversion of the  $SO_2$ . The platinized asbestos was prepared by soaking fine asbestos fibers in a saturated solution of  $H_2PtCl_6$  in water. The slurry was made basic with NaOH and then transferred to a large procelain evaporating dish. Most of the water was evaporated from the slurry by mild heating in a muffle furnace. Then enough formic acid was added to completely cover the

slurry and the temperature was raised to 400°C. This procedure produced Pt metal finely dispersed on the fibers. Finally, the asbestos was thoroughly washed with distilled water and dried in a muffle furnace.

#### 6. DETERMINATION OF THE CATALYTIC CONVERSION EFFICIENCY

The conversion efficiency of the converter was investigated by passing an SO<sub>2</sub>-air mixture through the converter and then through a midget impinger containing a known concentration of I<sub>2</sub> in a saturated KI solution.

The concentration of the SO<sub>2</sub> was first measured by passing it through the unheated converter and then through the I<sub>2</sub>-KI solution. Starch was added when the I<sub>2</sub> solution was pale yellow. The end-point was taken at the first disappearance of the blue color of the starch-I<sub>2</sub> complex. The volume of gas collected was measured with a wet-test meter. Five measurements of the SO<sub>2</sub> concentration gave a mean result of 98 ppm with a relative standard deviation of 8 percent. The temperature of the tube furnace was then maintained at 450°C as measured with a thermocouple. Ten liters of the gas were passed through the converter and collected in the I<sub>2</sub>-KI solution. The I<sub>2</sub> left was determined by adding a known amount of As<sub>2</sub>O<sub>3</sub> solution and back titrating the excess As<sup>+3</sup> with standard I<sub>2</sub> solution using starch as an indicator. This gave a result of 4.4 ppm of SO<sub>2</sub> which indicates a conversion yield of 93.5 percent SO<sub>3</sub>. Similar measurements on an SO<sub>2</sub>-air mixture containing 1900 ppm SO<sub>2</sub> gave conversion

yields ranging from 82 to 90 percent but the conditions were not necessarily optimum.

#### 7. SUGGESTION FOR FUTURE WORK

The catalytic method has been shown to be a more desirable and practical way of producing  $\text{SO}_3$  for  $\text{H}_2\text{SO}_4$  aerosols. However, further study is warranted to determine conversion efficiency yields at the 0.4 ppm level. Other important variables which may need to be considered for characterizing the performance of such a system are listed as follows:

1. Characterization of particle-size distribution via light-scattering techniques.
2. Collection efficiency of  $\text{H}_2\text{SO}_4$  aerosols on filters.
3. Development of analytical measured systems for analysis  $\text{H}_2\text{SO}_4$  aerosols (e.g. acid-base titration, conductivity).

## APPENDIX B

### REFERENCES

- <sup>1</sup>Mader, P. P., Hamming, W. J., and Bellin, A., *Anal. Chem.* 22, 1181-1183 (1950).
- <sup>2</sup>Contarel, L., Matijevic, E., Kerker, M., and Huang Chao-Ming, *J. Colloid and Interface Science* 24, 338-343 (1967).

FIGURE I  
SYSTEM FOR GENERATING SULFURIC ACID AEROSOL

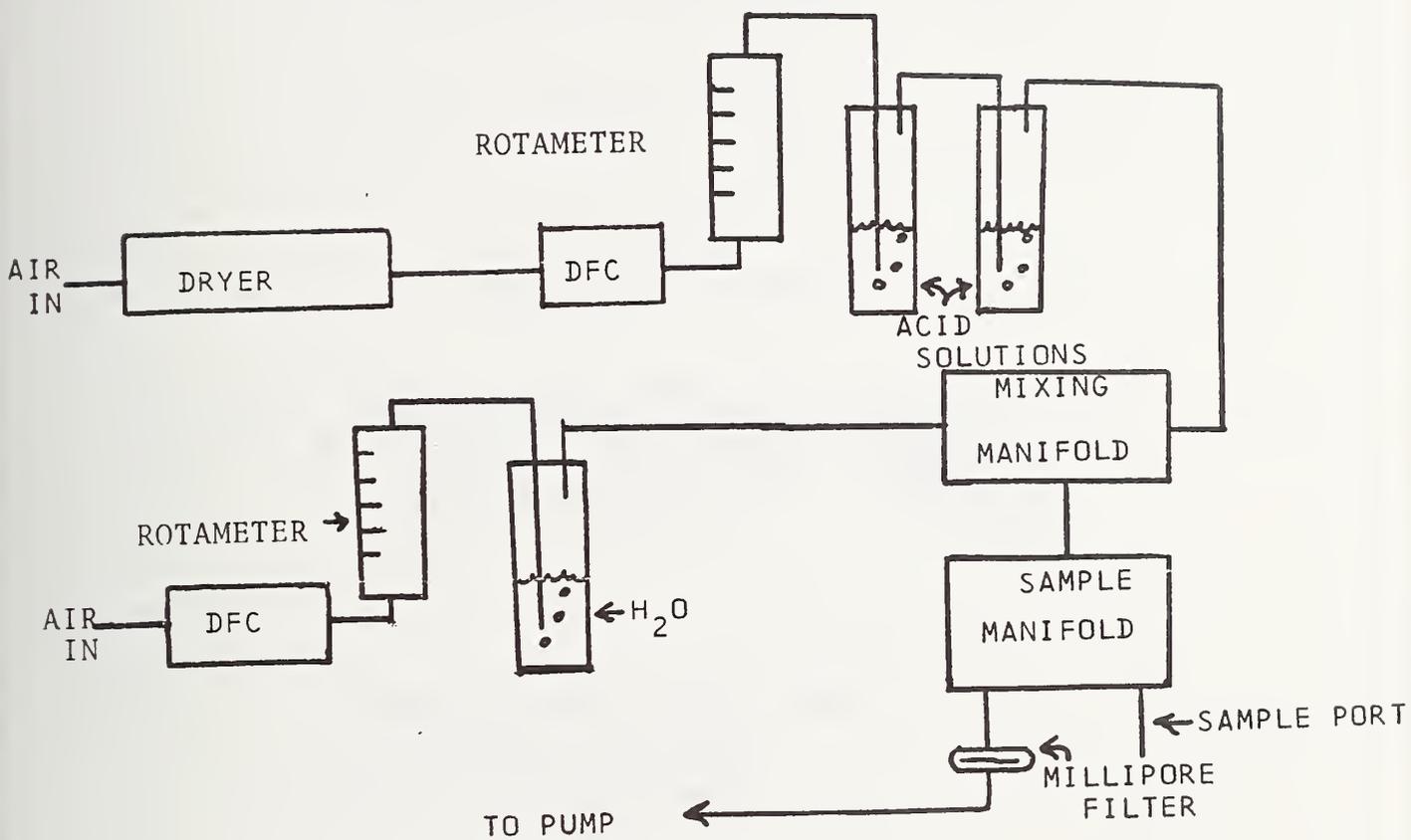
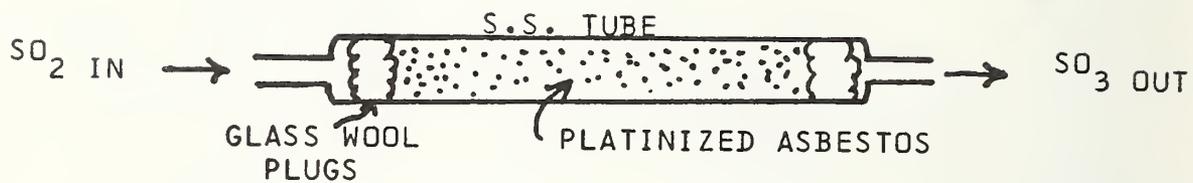


FIGURE 2  
CATALYTIC CONVERTER



TUBE PLACED IN TUBE FURNACE  
AND KEPT AT CONSTANT  
TEMPERATURE I.E. (350-450)

APPENDIX C

Progress Report

on

A Gas-Blending System for Phosgene in Air

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## 1. INTRODUCTION

This report summarizes the activity to date on a gas-blending system for producing known concentrations of phosgene ( $\text{COCl}_2$ ) in the range from 0.05 to 0.5 ppm. This work describes: (a) the preparation of phosgene-air and phosgene-nitrogen bulk mixtures in the range from 5 to 1700 ppm, (b) the investigation of a number of analytical methods for phosgene characterization and (c) the evaluation of a gas-blending system for producing phosgene concentrations from 0.05 to 0.5 ppm. A study of the stability of the phosgene-nitrogen bulk mixture is still in progress.

## 2. PREPARATION OF PHOSGENE BULK MIXTURES

Initial gas mixtures were prepared by adding phosgene gas sampled from above the liquid (Matheson Co.) at a partial pressure of 20 mm Hg to a large cylinder and then filling it with air to 500 psi. This yielded a concentration of 784 ppm. Similarly, a concentration of 1700 ppm of phosgene-in-nitrogen was prepared by adding 110 mm of phosgene to a cylinder and filling it to 1200 psi with "super-dry" nitrogen. To confirm the purity of the phosgene gas used to prepare these bulk mixtures, infra-red analysis of these mixtures was performed. A spectrum of the 784 ppm bulk mixture is shown in Figure 1. This spectrum was compared with a reference spectrum of 1.5 mm partial pressure of phosgene (99.5 + percent, redistilled from U. S. Naval Ordnance Test Station, Chemical Division, China Lake, California). The absorbances at A ( $5.5 \mu\text{m}$ ) and B ( $12 \mu\text{m}$ ) are prominent phosgene lines. The  $\text{CO}_2$  at  $4.3 \mu\text{m}$  and the  $\text{H}_2\text{O}$  vapor 2.5-2.7

microns are believed to be present in the added air. IR analysis of the phosgene-nitrogen mixture, however, showed no water vapor or HCl absorbances. To remove the possibility of hydrolysis of the phosgene in the phosgene-air bulk mixture because of the H<sub>2</sub>O vapor present, more dilute bulk mixtures were prepared by successive dilution of the 1700 ppm phosgene-nitrogen mixture with "super-dry" nitrogen. In table 1 is a comparison of the values obtained by pressure measurements with the values obtained by chemical analysis. These results show that a phosgene-nitrogen bulk mixture at the 5 ppm level can be prepared by successive dilution of a high concentration bulk mixture with no apparent loss of phosgene.

TABLE 1

Preparation of a 5 ppm Bulk Mixture by Successive  
Dilution of 1773 ppm Mixture

Calc'd Conc. COCl <sub>2</sub> (Press. Meas.)	Conc. COCl <sub>2</sub> Found (Cl <sup>-</sup> Meas.) (Mean)	Percent Deviation
		$\frac{\text{Calc'd}-\text{Found}}{\text{Calc'd}} \times 100$
1773 ppm	1683 ppm (3)*	+5.0
405 ppm	381 ppm (6)	+5.9
59 ppm	61 ppm (5)	-3.4
5.3 ppm	4.9 ppm (4)	+7.5

\*The number in parentheses represents the number of measurements made at each level.

### 3. DESCRIPTION OF ANALYTICAL PROCEDURES

One approach used in this work to analyze phosgene in mixtures is to absorb the phosgene quantitatively in a solution containing

50 percent methanol (MeOH) and 0.1 M KOH. The phosgene is completely hydrolyzed according to the reaction:



The resulting chloride concentration can then be measured using a variety of methods. Three methods for measuring the chloride concentration were investigated in this work and consisted of potentiometry, coulometry, and titrimetry using mercuric nitrate.

### 3.1 Potentiometry

The chloride concentration was measured potentiometrically using either an ion-selective chloride electrode or an Ag, AgCl electrode prepared in our laboratory. The reference electrode was a calomel electrode where contact with the analyte solution was made with a potassium nitrate salt bridge. A calibration curve was prepared by measuring known concentrations of KCl prepared in 50 percent MeOH-0.1 M KOH solution. The curve was linear from  $10^{-4}$  to  $10^{-1}$  M  $\text{Cl}^-$ . A problem found in the application of this method is that the electrode response was sluggish in this alcoholic medium. The time required for the electrodes to reach equilibrium varied from 1/2 to two hours and was considered impractical for measuring phosgene in mixtures for this work.

### 3.2 Coulometry

A commercially available automatic coulometric titrator was used to analyze the chloride concentration. The phosgene was collected as already described in 50 percent, MeOH-0.1M KOH solution. This solution were titrated with electrogenerated silver ion. The titrator was calibrated by plotting the time in seconds

required to titrate known concentrations of KCl in 50 percent MeOH-0.1M KOH solution. A typical calibration curve is shown in Figure 2. This method was used to determine the phosgene concentration of gas mixtures from 5 to 1700 ppm. The concentration of phosgene in ppm in the gas mixture was calculated as follows:

$$C_v = 1/2 \frac{M E}{V}$$

where

$C_v$  = concentration of phosgene in ppm in gas mixture.

M = moles of chloride  $\times 10^{-6}$  found in total volume of absorbing solution.

E = molar volume of gas and is 24.5 liters/mole at 25 °C.

V = volume of gas mixture collected in absorbing solution in liters.

### 3.3 Titrimetry using Mercuric Nitrate

Chloride ion can also be titrated with a standard solution of mercuric nitrate (0.005 N) in a 90 percent alcohol-10 percent water solution (1). In this procedure, a mercuric nitrate solution is standardized with known chloride concentration in a 90 percent alcohol-10 percent water solution at an apparent pH of 3.6 in the presence of diphenylcarbazone as indicator. The mercuric nitrate forms undissociated mercuric chloride, until an excess of mercuric ions appear, which then combine with the indicator to form a violet-colored complex, thus marking the end-point in the titration. The sensitivity of this method is sufficient for the determination of a 5 ppm phosgene bulk mixture when 10 to 20 liters of the mixture is collected in a 5-10 ml volume of 50 percent MeOH-0.1 M KOH

absorbing solution. The concentration of the phosgene in the bulk mixture is obtained by using the equation:

$$C_v = \frac{T \times v \times E}{2 MV}$$

where

$C_v$  = concentration of phosgene in ppm in bulk mixture.

T = titer of mercuric nitrate solution (i.e.  $\mu\text{g Cl}^-$  equivalent to 1.0 ml of  $\text{Hg}(\text{NO}_3)_2$  solution).

v = volume of titrant used to titrate the  $\text{Cl}^-$  in the total volume of the absorbing solution in ml.

M = molecular weight of  $\text{Cl}^-$ .

E = molar gas volume, which is 24.5 liters/mole at 25 °C.

V = volume of phosgene bulk mixture collected in liters.

### 3.4 Spectrophotometric Determination of Phosgene with 4-P-nitrobenzylpyridine and N-benzylaniline Reagent

The lack of specificity of methods which solely measure chloride ion is a drawback in determining the stability of phosgene-nitrogen bulk mixtures and in evaluating the performance of a gas-blending system. For this reason a specific method for phosgene analysis was sought to aid in these studies. Perusal of the literature revealed a number of spectrophotometric methods which have been used to measure phosgene in air mixtures. However, almost all of those reported indicate some interference of HCl (a common hydrolysis product of phosgene) and other mineral acids. Recently, Noweir and Pfitzen (2) have reported on the spectrophotometric

determination of phosgene in air below 0.1 ppm. The absorbing reagent consisted of 0.25 percent 4-p-nitrobenzylpyridine (NBP) and 0.5 percent N-benzylaniline (BA) in diethylphthalate. These authors found no affect of water vapor, HCl, Cl<sub>2</sub>, CO<sub>2</sub>, and other vapors commonly found in industrial atmospheres on the color development of this reagent with phosgene. Therefore, this method was investigated in this work to detect any decomposition of phosgene either in the bulk mixture or in the manifold of the gas blending system.

#### 4. EVALUATION OF A GAS-BLENDING SYSTEM FOR PRODUCING PHOSGENE CONCENTRATIONS IN AIR FROM 0.05 to 0.5 PPM

A gas-blending system for producing phosgene concentrations by dilution of a 4.6 ppm bulk mixture in the range from 0.05 to 0.5 ppm was evaluated. The phosgene bulk mixture and diluent air were admitted into the gas-blending system at precisely controlled flow rates. The phosgene concentration of the diluted mixture in the sampling manifold was determined by passing a known volume through 5-ml of the NBP-BA reagent at a rate of 0.5 l/min, waiting five minutes for color development, and then measuring the absorbance versus an NBP-BA reagent blank at 475 nm. A calibration plot was prepared by collecting known volumes of the phosgene bulk mixture in 5-ml of the NBP-BA reagent and measuring the absorbances. A typical calibration plot is presented in Figure 3. Note that this curve is non-linear above 4 µg COCl<sub>2</sub>/ml (i.e. A=0.4) and demonstrates a negative deviation from the Lambert-Beer law. The phosgene con-

centration of the bulk mixture was determined coulometrically and gave an average result of  $4.6 \pm 0.1$  ppm. The results obtained using the dilution system are plotted in Figure 4 and summarized in Table 2.

TABLE 2

Calculated vs. Observed Phosgene Concentrations  
in Sampling Manifold

Flow Rate Bulk Mixture 1/min	Flow Rate Diluent 1/min	Dilution Factor	Calc'd Conc. ppm	Obs. Conc. ppm	(Calc'd-Obs.) Deviation in ppm
0.237	0.255	0.4817	2.2	2.2	0.00
0.122	0.380	0.243	1.1	1.1	0.00
0.060	0.440	0.120	0.55	0.55	0.00
0.0329	0.491	0.0628	0.29	0.29	0.00
0.101	3.06	0.0320	0.15	0.13	+0.020
0.0329	3.06	0.0107	0.049	0.046	+0.003

These results indicate that dilutions of the phosgene bulk mixture via the gas-blending system to produce concentrations from 0.05 to 0.5 ppm are accurate.

5. STABILITY OF THE PHOSGENE-NITROGEN BULK MIXTURE

The phosgene-nitrogen bulk mixture at the 5 ppm level was measured coulometrically over a period of three months and the results are presented in Table 3. These results indicate no significant decrease in the phosgene concentration over this time period. Because of the non-specificity of the coulometric method, the spectrophotometric technique using NBP-BA reagent was developed to investigate any change in the phosgene concentration. One way to determine

whether any decomposition of phosgene has occurred is to absorb a known volume of the bulk mixture in the NBP-BA reagent, and then extract the phosgene from the complex quantitatively followed by the coulometric measurement of chloride. This was accomplished by the following procedure:

Forty liters of the bulk mixture was collected in 5-ml of NBP-BA reagent. A 3.0 ml aliquot was placed in a separatory funnel and shaken with an equal volume of methanol-KOH solution. This solution was allowed to stand for 1-2 hours to decompose the phosgene complex, and 5-ml of distilled water was added. The mixture was shaken and the diethyl phthalate was separated from the alcohol-water phase. The organic layer was acidified with a few drops of concentrated nitric acid and washed with 5-ml of H<sub>2</sub>O. The wash water was then separated from the organic layer and added to the alcohol-water phase from the first extraction. The organic layer was checked for chloride ion by adding a few drops of CH<sub>3</sub>OH-AgNO<sub>3</sub> solution. A negative test was obtained. The alcohol-water phase containing the chloride ion was transferred to a 25.0 ml volumetric flask and filled to the mark with 50 percent CH<sub>3</sub>OH-0.1N KOH solution. A 6-ml aliquot of this solution was then titrated coulometrically. The average of two determinations was 4.2 ppm. This value compares favorably with the value of 4.6 ± .1 ppm obtained on the bulk mixture determined previously by coulometry. Hence, these results indicate that the phosgene

bulk mixture is sufficiently stable. Additional measurements are still in progress to detect any change in the phosgene concentration in the bulk mixture by following the absorbance of the NBP-BA-phosgene complex with time.

TABLE 3

Study of the Stability of Phosgene-Nitrogen  
Bulk Mixture

<u>Time, Days</u>	<u>Apparent COCl<sub>2</sub> Conc. ppm</u>
4	4.9 ± .1
82	4.5
89	4.7
95 (3 months)	4.6 ± .1

APPENDIX C

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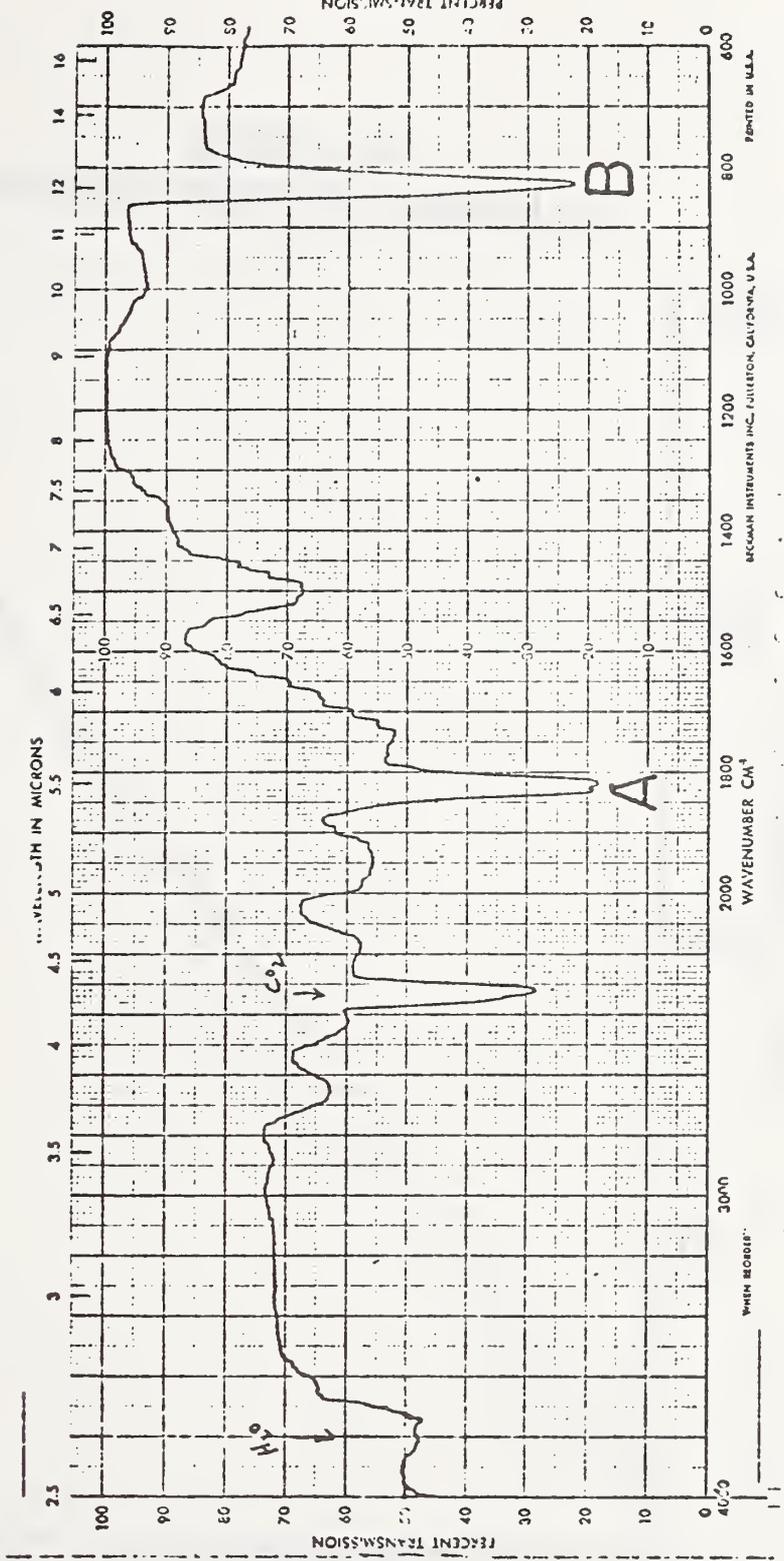
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10

FIGURE 1

INFRA-RED SPECTRUM OF PHOSGENE in AIR



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BECKMAN INSTRUMENTS INC. FULLERTON, CALIFORNIA, U.S.A.

WAVENUMBER CM<sup>-1</sup>

WAVELENGTH MICRONS

SPECTRUM NO. #1  
 DATE 3/29/75  
 SOURCE 670 mm. COCl<sub>2</sub>  
 in air 784 ppm  
 SOURCE \_\_\_\_\_  
 STRUCTURE \_\_\_\_\_  
 PATH \_\_\_\_\_ mm  
 SCALAR \_\_\_\_\_  
 CONCENTRATION \_\_\_\_\_  
 PRESSURE \_\_\_\_\_  
 COMMENTS \_\_\_\_\_  
 \_\_\_\_\_  
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**Beckman**  
 INFRARED  
 SPECTROPHOTOMETER

FIGURE 2  
CALIBRATION FOR PHOSGENE

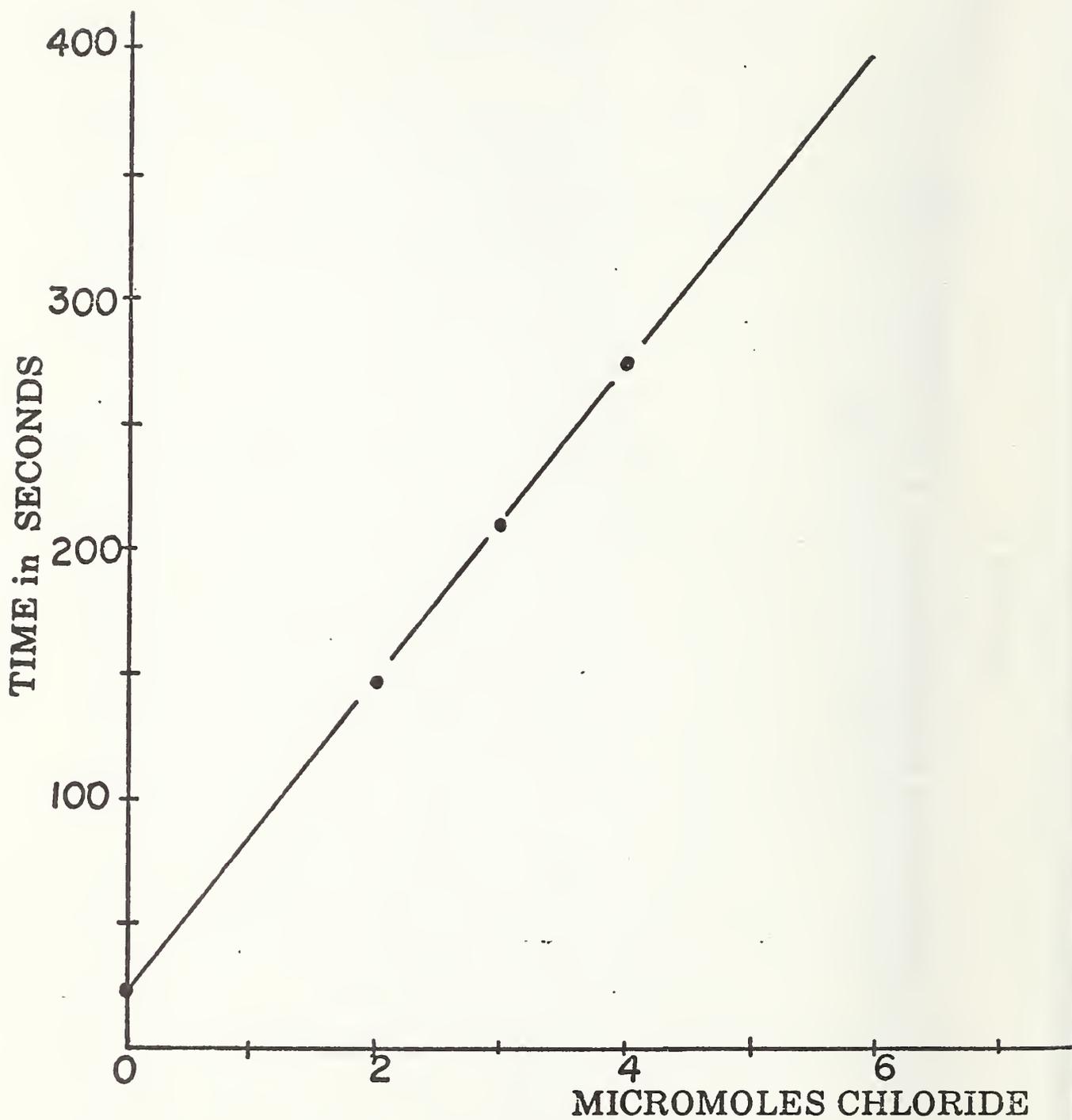


FIGURE 3  
CALIBRATION FOR PHOSGENE

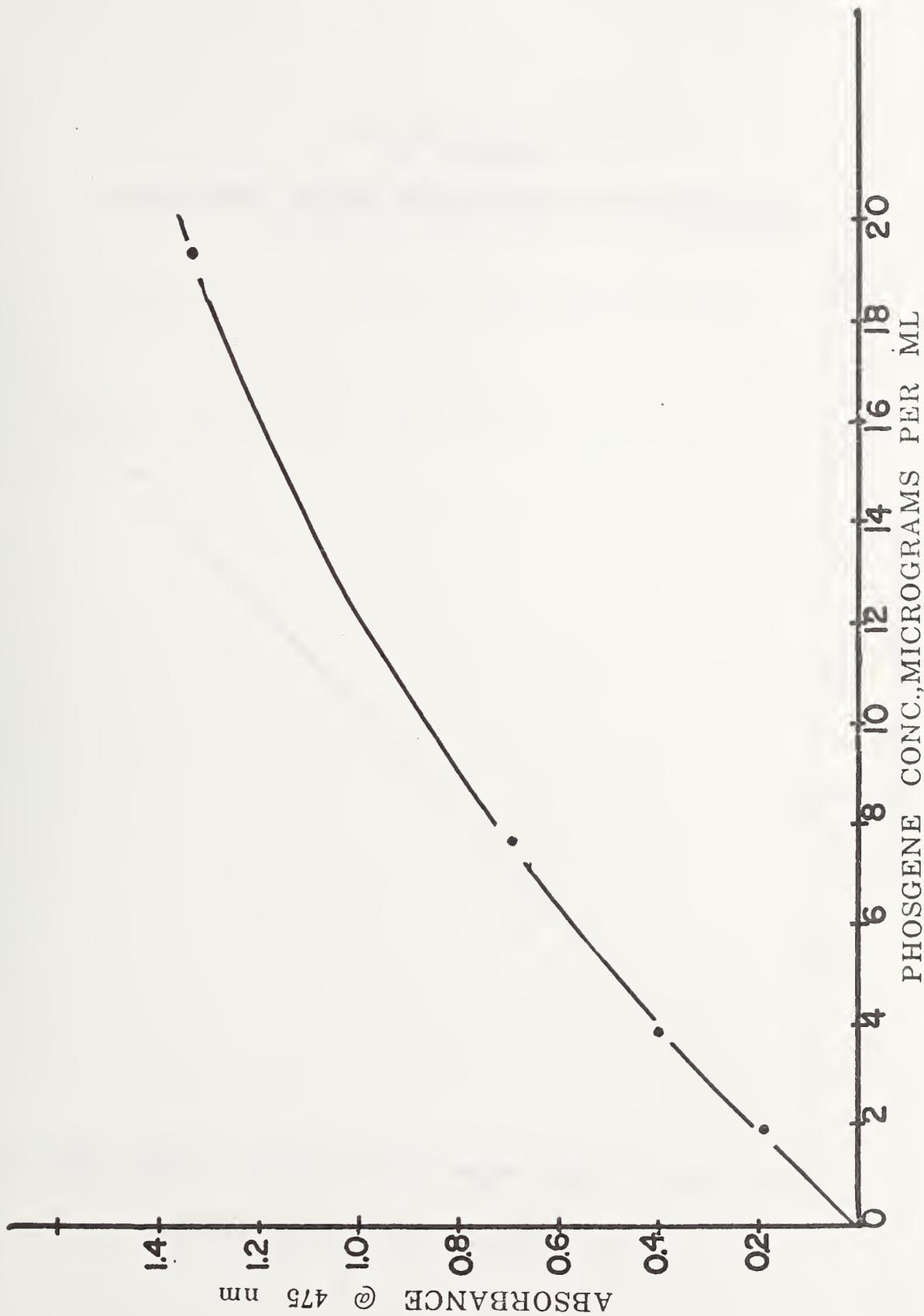
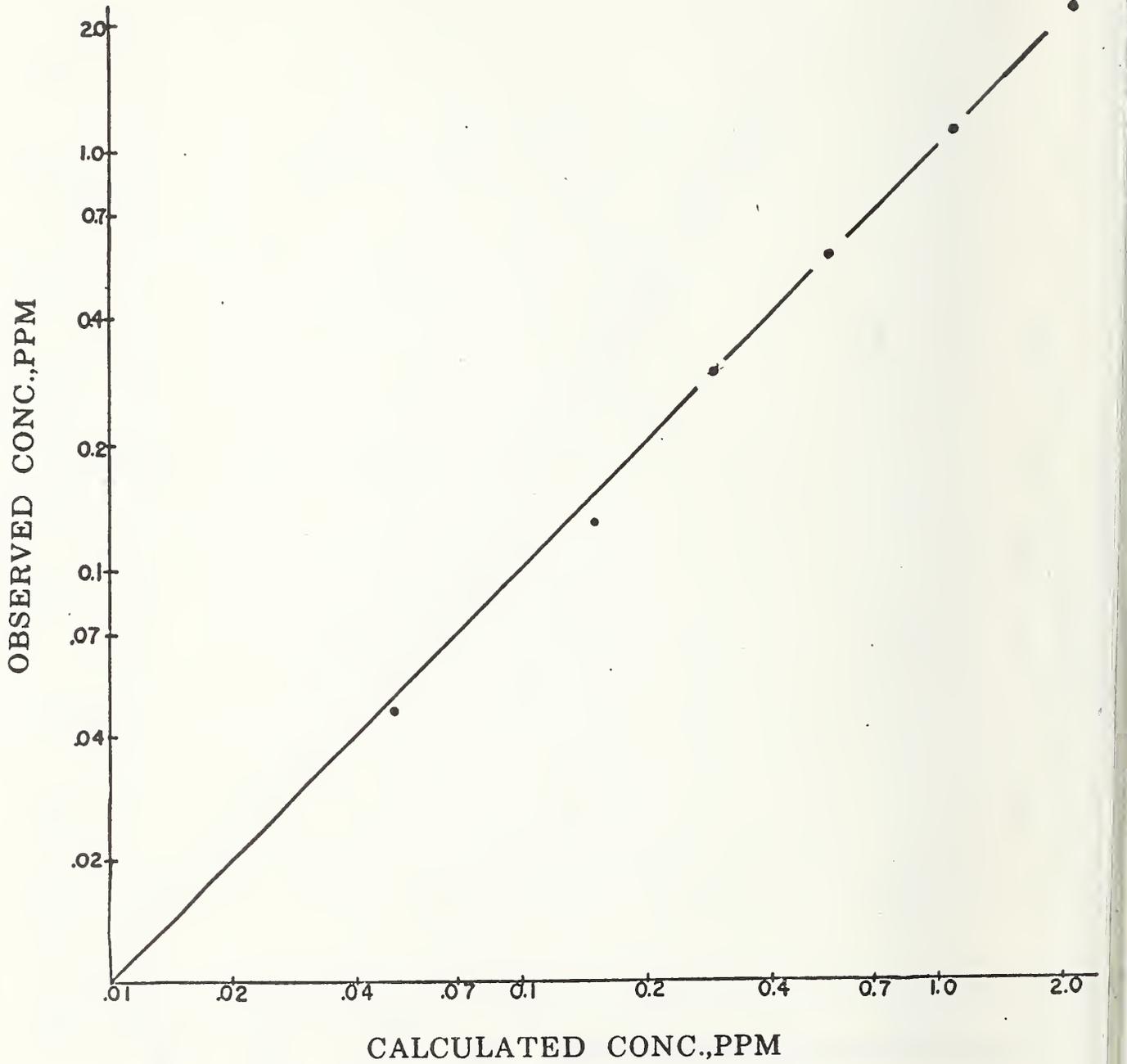


FIGURE 4  
DILUTION OF PHOSGENE BULK MIXTURE



APPENDIX D

Progress Report

on

TDI and MDI Vapor Generation and Dilution System

E. P. Scheide, E. E. Hughes and J. K. Taylor



## A. INTRODUCTION

This report describes experimentation performed in the development of a generation system and method of analysis of test atmospheres of toluene diisocyanate (TDI) and methylene diphenyl isocyanate (MDI). Also, suggestions for future work are included.

## B. EXPERIMENTAL

### 1. Analytical Systems

Several different analytical systems were considered for use in the analysis of TDI and MDI vapors. These were: (1) colorimetric, (2) gas chromatography, and (3) infrared spectroscopy. The most common method in use is that originally proposed by Marcali<sup>4</sup> for the determination of TDI in air, and subsequently modified by other workers.<sup>5,6</sup> This colorimetric method depends on the hydrolysis of the TDI to the corresponding amine; the latter is diazotized and finally coupled with N-1-naphthylethylenediamine to form a colored complex, which is measured photometrically. This method was not used in our experimentation because it does not differentiate between TDI and the diamine that is formed upon the hydrolysis of TDI.

Infrared spectroscopy has also been used for the analysis of isocyanates,<sup>7,8</sup> but the sensitivity is too low for the proposed applications.

The analytical method finally chosen for this work was gas chromatography using a flame ionization detector. Sampling can be easily performed with this technique, it possesses

adequate sensitivity, and separation and identification of the different isocyanates and their reaction products can be achieved. Even more sensitivity can be achieved if desired using an electron capture detector. The most satisfactory column was a 6 ft., 10 percent VC-W.98, 80-100 WHP column.

## 2. Generation Systems

Several different types of generation systems were investigated and these are summarized below:

a. Pressurized Cylinders. Mixtures of TDI vapor in air, nitrogen, and super dry nitrogen were made and placed in pressurized steel cylinders. The TDI vapor from these cylinders was always much less than the calculated concentration and contained several reaction products. The TDI was apparently both adsorbing onto the walls of the cylinder and decomposing. Experiments were also performed using pre-conditioned cylinders with similar results. Another problem associated with the use of pressurized cylinders is that the bulk mixture needed of TDI is of extremely low concentration. It might be possible to make stable cylinder mixtures of TDI in nitrogen at higher TDI concentrations.

b. Liquid Saturators. The next generation technique investigated was that of using a liquid saturation system. This consists of an impinger containing TDI through which is passed a stream of clean, dry nitrogen. A diagram of this saturator is shown in Figure 1.

The major difficulty in preparing TDI in air mixtures by this method was contamination by volatile impurities. Even though the impurity concentration in the liquid phase may be very low,

problems are still encountered because of the extremely low vapor pressures of TDI and MDI. This causes the effective vapor phase concentration of the volatile impurities to be much higher. If these impurities interfere with the analytical determination, then they must be completely removed. To illustrate this problem, if a TDI sample contains 99.97 percent TDI and 0.03 percent toluene in the liquid phase, the vapor phase will contain approximately equal concentrations of TDI and toluene because the vapor pressure of toluene is 3000 times that of TDI.

Once the volatile impurities are removed, however, this could be an effective method for generating TDI in air. This method was set aside because of the hazard associated with handling large quantities of TDI. It is felt that the TDI/silica gel column presents far less of a hazard while being just as effective as a generation system for TDI.

c. TDI/Silica Gel Column. To minimize the hazard in case of accident, the liquid saturation technique was abandoned and replaced by a TDI/silica gel "column". This "column" consists of a piece of stainless steel tubing 3/8 inch in diameter and 25 inches in length. The "column" was packed with silica gel (6-16 mesh, grade 05) which had been soaked in purified TDI for 30 minutes. The "column" was bent into a loop and on-off valves were attached at both ends. As dry air is passed through the "column" the liquid phase (TDI) "bleeds" off of the column in a constant and reproducible manner.

Prior to use, the "column" must be conditioned for several hours by passing a slow stream of dry air through it. This will remove any remaining volatile contaminants and simultaneously coat the entire inside surface of the column with TDI. After this conditioning process, the column will emit a reproducible mixture of TDI in air. The reproducibility of the system has been checked several times 1-2 weeks apart resulting in daily reproducibility of  $\pm 3$  percent and weekly reproducibility of  $\pm 6$  percent.

A study was made of the effect of the flow rate of air through the column upon the concentration of TDI emitted. The results of this study show that the concentration of TDI remains constant ( $\pm 1$  percent) using air flows between 1.5 and 5.5 liters per minute with increasing concentrations at lower flow rates.

The column saturation technique was evaluated by chromatographic analysis, using liquid standards of various concentrations (TDI in toluene), and was found to produce TDI concentrations of 4.6-5.0 ppm TDI. This concentration is less than that produced by the liquid saturation technique (13 ppm) and may be caused by an affinity of the TDI for silica gel thereby lowering its effective vapor pressure, a pressure drop through the column causing the concentration to decrease, or other reasons.

d. MDI. According to reports in the literature,<sup>4,9-12</sup> and preliminary experimental investigations, MDI possesses too

low a vapor pressure to be generated in the gaseous state at the concentrations of interest at room temperature. Its danger occurs when it is in the form of an aerosol or a fine dust particle. An MDI "column" similar to the TDI "column" was constructed and evaluated but without success. Because of these reasons, the development of an MDI gas generation system has been delayed until more information can be obtained and the decision made as whether or not to attempt the development of an apparatus for the generation of MDI aerosols and dusts.

### 3. The Dilution System

The TDI column has been used in conjunction with a dilution system to produce lower concentrations of TDI in air, but with limited success. Several breadboard arrangements have been tried, but more work is needed in this aspect of the problem. The TDI coming out of the system is of much lower concentration than calculated. Several suggestions are included on the possible causes of this problem and directions for future experiments.

### 4. SUGGESTIONS FOR FUTURE WORK:

The following are suggestions for future experiments to be performed.

#### 1. New Dilution System

A new dilution system should be built to minimize the internal surface area. Figure 2 shows a diagram of a mixing manifold with low surface-to-volume ratio that would be

incorporated into the system.

2. Longer Equilibration Time

The dilution system should be conditioned for much longer times. It has been suggested,<sup>4,9</sup> that as long as 72 hours equilibration time is needed. Minimizing the internal surface area of the dilution system should also shorten this equilibration time.

3. Dry Air

The use of super-dry air might also reduce losses of TDI in the system.

4. Non-Adsorbing Materials

If the column and dilution system could be constructed of materials that did not adsorb TDI the problem would be solved.

## APPENDIX D

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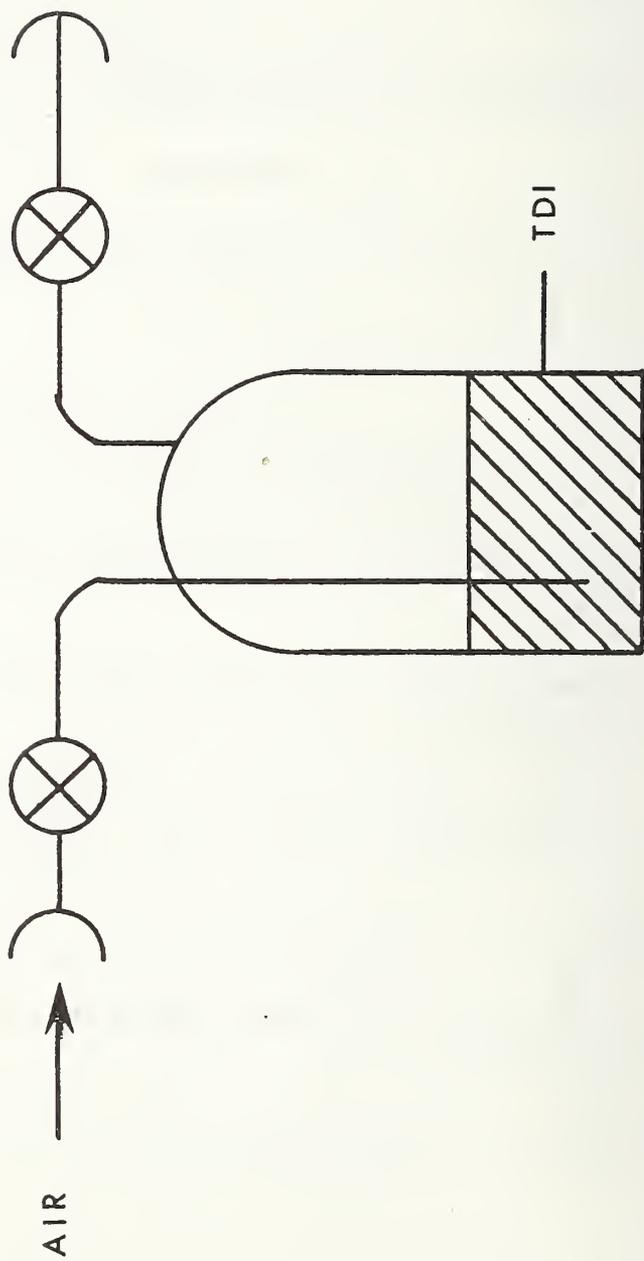


Figure 1. Liquid Saturator

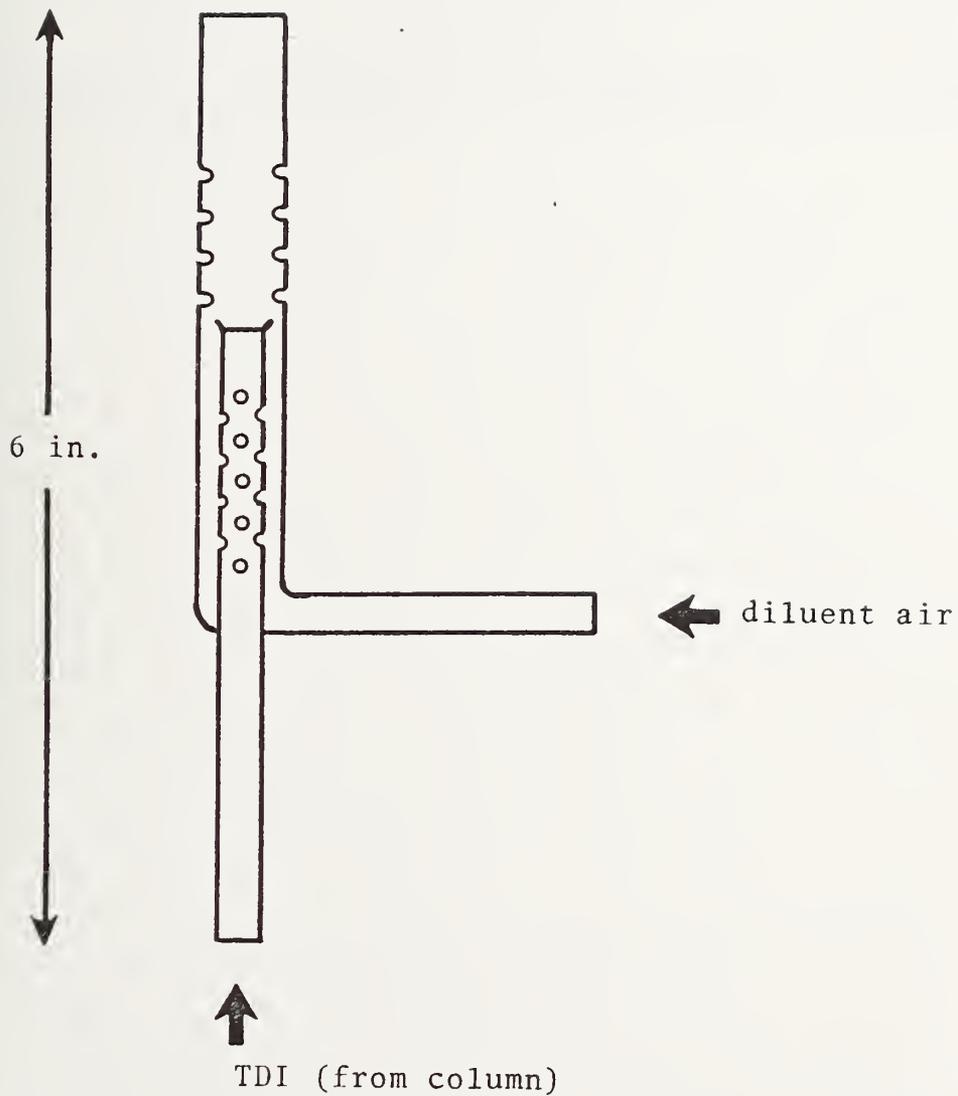


Figure 2. Proposed TDI Mixing Manifold



APPENDIX E

Progress Report

on

The Formaldehyde Generation and Dilution System

A. A. Angotti, E. P. Scheide, E. E. Hughes, and J. K. Taylor

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## A. INTRODUCTION

This progress report describes experimentation performed in the development of a generation and dilution system and method of analysis of test atmospheres of formaldehyde. Also, suggestions for future work are included.

## B. EXPERIMENTAL

### 1. Analytical Systems

The analytical systems considered for the analysis of formaldehyde-air mixtures were gas chromatography<sup>1-4</sup>, and a chromotropic acid colorimetric method.<sup>5-8</sup> Gas chromatography provided good selectivity but the sensitivity was not sufficient for analysis of the lower concentration mixtures. For this reason, the chromotropic acid colorimetric procedure was used. The air sample was bubbled through the reagent and the resulting color change was monitored by use of a spectrophotometer. A probe colorimeter has been obtained and this will be used in the analytical system in order to monitor the formaldehyde concentration output of the system continuously.

### 2. Generation Systems

Several types of formaldehyde generation systems were investigated and these are summarized below:

a. Pressurized Cylinders. Mixtures of formaldehyde (obtained by passing a slow stream of the diluent over para-formaldehyde supported on asbestos) in air, nitrogen and super-dry nitrogen were made and placed in pressurized steel cylinders.

These mixtures proved unsatisfactory because the analyzed concentration was always far less than calculated. Also, the mixtures were not stable and decayed rapidly with time.

b. Liquid Saturator. Another way of generating mixtures of formaldehyde in air is to bubble air through an impinger containing formalin solution. This technique was abandoned because of the large amounts of water, methanol and other substances that accompanied the formaldehyde.

c. Paraformaldehyde. Two systems were used to produce formaldehyde from paraformaldehyde. These are shown schematically in Figure 1. They were about equal in efficiency and stability. The output of the generator was fed directly into a mass spectrometer and while operating at room temperature only a formaldehyde peak was observed. On the other hand, when the temperature was increased, in order to increase the formaldehyde concentration, other peaks appeared in the spectrum. Also, the paraformaldehyde vaporized and later condensed downstream from the generator. For these reasons, this generator system can only be used near room temperature.

The range of formaldehyde concentrations obtainable with this system is from 0.5 ppm to about 60 ppm. The major drawback, however, is the increasing instability and unpredictability at the higher formaldehyde concentrations. For example, the precision at 1 ppm is  $\pm 1$  percent, at 10 ppm  $\pm 4$  percent, and at 50 ppm  $\pm 30$  percent. The stability is good for 24 hours and longer at the

lower formaldehyde concentrations.

The time to reach equilibrium increases with increasing formaldehyde concentration, and at the higher concentrations, the system does not appear to reach equilibrium.

### 3. The Dilution System

A standard dilution system was modified for use with the formaldehyde generator. A schematic of this system is shown in Figure 2.

## C. SUGGESTIONS FOR FUTURE WORK

The following are suggestions for future experiments to be performed.

### 1. Effect of Flow Rate

Further experiments should be performed to investigate the relationship between the formaldehyde and diluent flow rates. It is possible that other flow combinations might increase the precision of the generator output.

### 2. Effect of Temperature

Further studies should be conducted on the effect of temperature on the stability of the system, especially slightly above and below ambient temperature.

### 3. Modified Dilution System

It might be possible to build a new dilution system of more inert materials that would reduce the interaction between formaldehyde and the walls of the system.

### 4. Effect of Equilibration Times

Longer equilibration times at the higher formaldehyde

concentrations might produce a more stable output. This should be investigated.

#### 5. Modified Analytical System

The new probe colorimeter will provide a tool to facilitate the investigation of the system including the identification of problem areas.

## APPENDIX E

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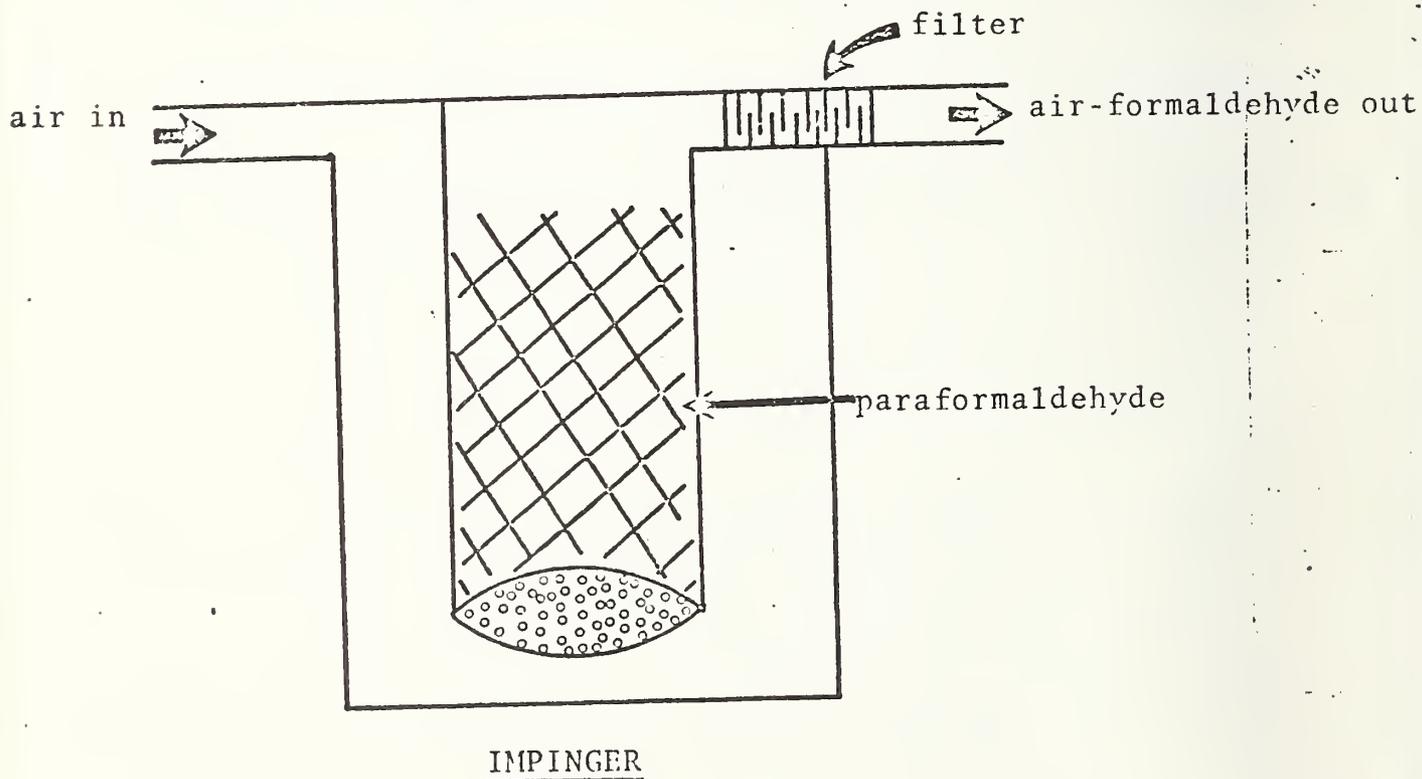
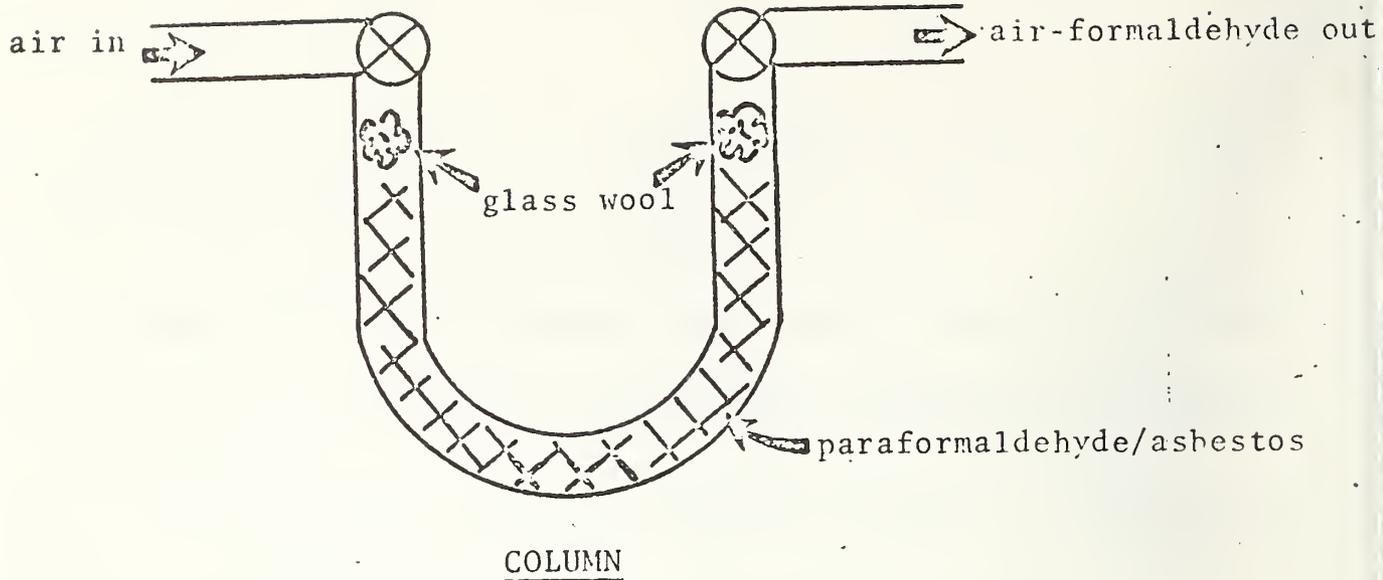


Figure 1. Formaldehyde Generation Systems

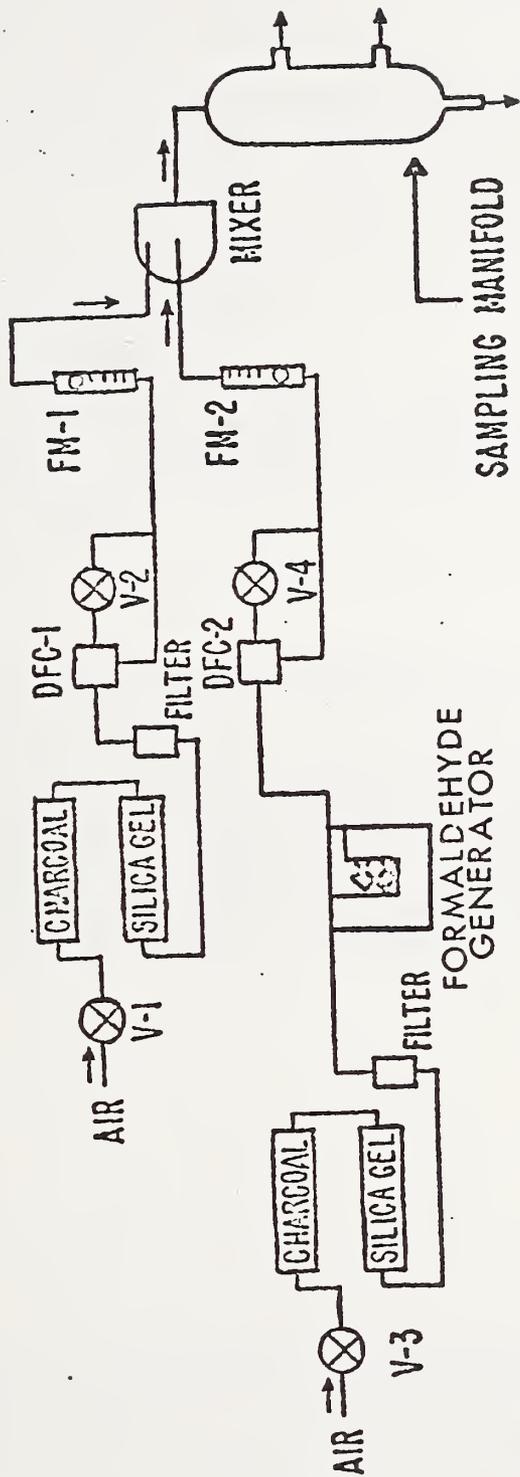


Figure 2. Formaldehyde Generation and Dilution System Schematic



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7. AUTHOR(S)  John K. Taylor	8. Performing Organ. Report No.  NBSIR 73-411		
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12. Sponsoring Organization Name and Complete Address (Street, City, State, ZIP)  National Institute for Occupational Safety & Health Division of Laboratories and Criteria Development Cincinnati, Ohio 45202		13. Type of Report & Period Covered  Interim Report	14. Sponsoring Agency Code
15. SUPPLEMENTARY NOTES			
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<p>17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)</p> <p>Chemical analysis; industrial hygiene; reference materials.</p>			
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