NBSIR 73-292

Gas Generation Systems for the Evaluation of Gas Detecting Devices

E. E. Hughes, W. D. Dorko, E. P. Scheide, L. C. Hall,
A. L. Beilby, and J. K. Taylor

National Bureau of Standards
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Final Report

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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

GAS GENERATING SYSTEMS
FOR THE
EVALUATION OF GAS DETECTING DEVICES

A Report to

National Institute for Occupational Safety and Health

by

E. E. Hughes, W. D. Dorko, E. P. Scheide, L. C. Hall
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GAS GENERATING SYSTEMS FOR THE EVALUATION OF GAS DETECTING DEVICES

ABSTRACT

This report summarizes a project concerned with the design, testing and calibration of systems for producing known low concentrations of a number of substances in air at concentrations in the vicinity of the TLV (Threshold Limit Value). The substances include carbon dioxide, carbon monoxide, ozone, sulfur dioxide, hydrogen sulfide, nitrogen dioxide, benzene, carbon tetrachloride, trichloroethylene, tetrachloroethylene, ammonia and chlorine. The systems are of four basic types: direct delivery from cylinders of known concentration, dynamic blending of high concentrations with air, permeation tubes and generation of the substance directly in an air stream. Monitoring systems are suggested to allow confirmation of the quantities generated. Details of construction are given.

Key words: Gas mixtures, gas detectors, trace gas analysis.

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1. INTRODUCTION

This report summarizes work concerned with the development of gas generation systems for use in verifying the performance of gas detection devices or for the calibration of gas analysis instrumentation. The systems were designed to provide mixtures of a number of different gases and vapors in air at concentrations representing fixed proportions of the Threshold Limit Value (TLV). Furthermore, they furnish a sufficient volume of gas to allow continuous testing of devices while maintaining a predetermined concentration level.

Several methods have been employed to achieve those purposes, the simplest of which is the utilization of stable gas mixtures. Those mixtures can be standardized and then used directly as calibrants. Alternatively, they can be incorporated into a reliable gas blending system and quantitatively diluted to produce dynamic calibrant mixtures of lower concentration. Gas mixtures of less than desirable long term stability can also be utilized if they are periodically re-analyzed. Another approach is the application of calibrated gas generators such as the ultra-violet ozone generator or permeation devices in a gas dilution system. In each instance an analytical system has been described or included as an integral part of the apparatus to provide a means of verifying the composition of the gas mixtures produced. The object, whenever possible, has been to provide traceability to the National Bureau of Standards by the use of NBS Standard Reference Materials. Where

Table 1.1. Substances and Concentrations Generated

Substances	TLV ppm	Concentration Range, ppm
Carbon Monoxide	50	25 — 250
Carbon Dioxide	5,000	2,500 — 25,000
Ozone	0.1	0.05 — 0.5
Sulfur Dioxide	5	2.5 — 25
Hydrogen Sulfide	10	5.0 — 50
Nitrogen Dioxide	5	2.5 — 25
Carbon Tetrachloride	10	5 — 50
Tetrachloroethylene	100	50 — 500
Trichloroethylene	100	50 — 500
Benzene	25	12.5 — 125
Ammonia	50	25 — 250
Chlorine	1	0.5 — 5.0

these are not presently available, NBS will furnish primary standards or perform calibrations as required, on a cost-reimbursable basis to insure traceability.

Table 1.1 lists the substances of initial interest to NIOSH, for which gas generation systems were developed. The systems are described in detail in the following sections of the report. The ranges of concentrations generated by the systems for these substances and the Threshold Limit Value (TLV) are also shown in Table 1.1.

2. GAS CYLINDER SAMPLING APPARATUS

(CO, CO_2)

A. Introduction

A number of gas mixtures have sufficient long term stability to allow direct use from cylinders without monitoring the concentration in the sampling manifold. Carbon monoxide and carbon dioxide are examples of gases that may be used in this way. The mixtures can be analyzed with an absolute accuracy of better than ± 2 percent. Storage of carbon dioxide mixtures for periods of one year will not result in reduction of the concentration through reaction or adsorption. Mixtures of carbon monoxide, however, should be reanalyzed at least every three months. Gas mixtures of carbon monoxide and carbon dioxide of the following composition have been prepared and analyzed, (Table 2.1):

Table 2.1 Concentration of CO and CO_2

Carbon Monoxide

Cylinder Number	Nominal Concentration ppm	Analyzed Concentration ppm
A-11191	25	25.0
A-11193	50	54.5
A-11167	100	99.2
A-11173	250	249

Carbon Dioxide

Cylinder Number	Nominal Concentration Mole Percent	Analyzed Concentration Mole Percent
A-11159	0.25	0.253
A-11145	0.50	0.493
A-11146	1.0	0.972
A-11150	2.5	2.43

B. Preparation for Use

The apparatus used with stable gas mixtures is shown schematically in Figure 2.1. Four gas mixtures in cylinders may be attached simultaneously and used successively. Each mixture is controlled by a valve on the front panel. The valve number corresponds to the inlet fitting at the rear of the cabinet. The flow into the manifold is measured by the flow meter. The only reason for this measurement is to insure that the flow of gas into the sampling manifold is greater than the sampling rate.

After attaching the appropriate number of cylinders to the inlets at the rear of the cabinet it is necessary to flush each line from the cylinder to the control valve on the panel. The cylinder must be equipped with a control valve of some kind. This may be in the form of a regulator with a shut-off valve or more simply, a control valve without regulator. The system is designed conservatively for a maximum pressure of 1500 psi. Gas mixtures will be supplied as needed at an initial pressure below 1500 psi so that a pressure regulator is not necessary. In any case, the control device on the cylinder should be flushed before attaching the line to the cabinet. After attaching this line, it should be flushed by bleeding gas from the cylinder through it with the valve on the panel open. After a few hundred cubic centimeters of gas have passed, the control

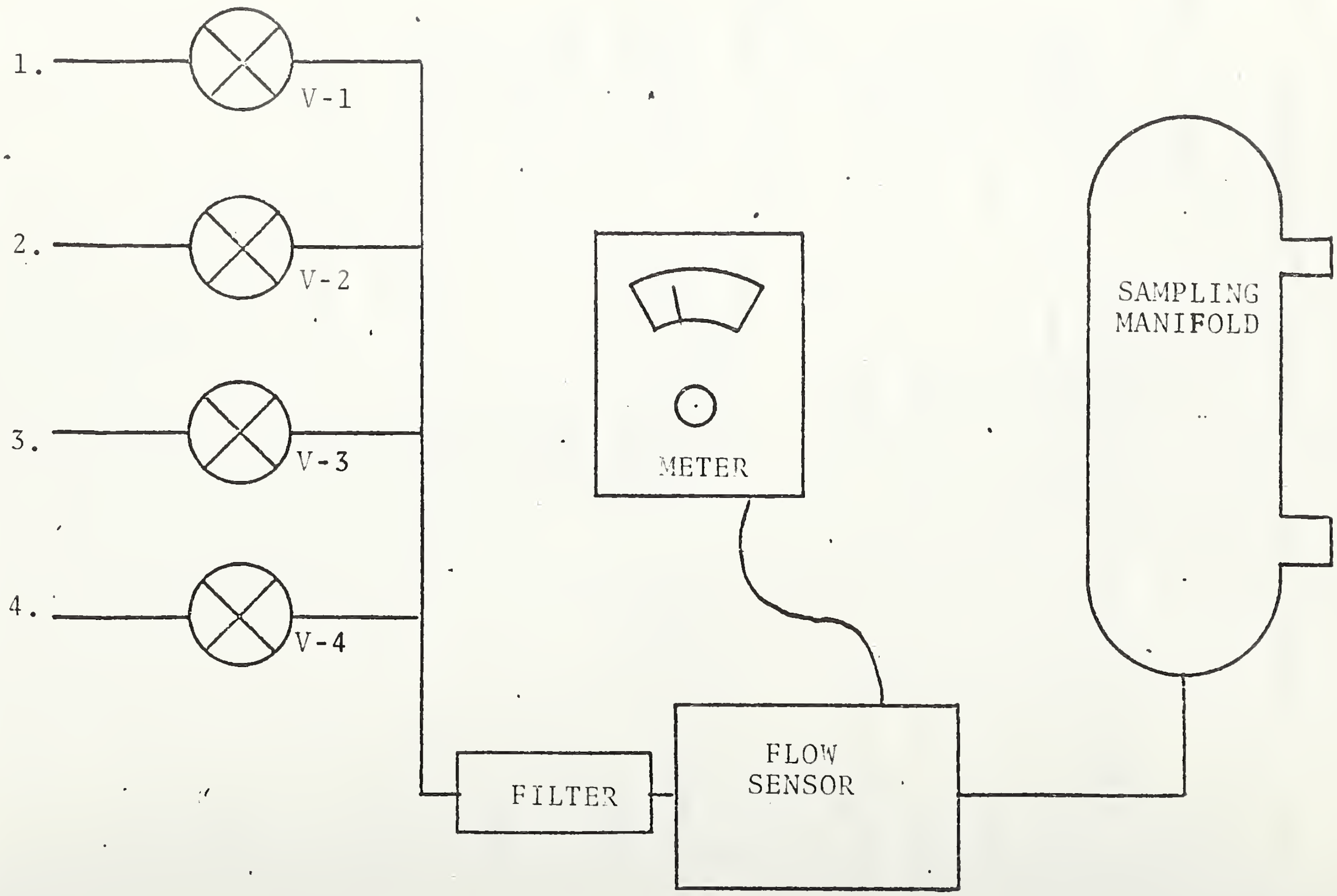

Figure 2.1 Schematic of Cylinder Sampling Apparatus.

valve on the panel should be closed. With this valve closed, there should be no indication of flow by the flow meter. Repeat this procedure with each cylinder. The system is now ready for use.

C. Use of the Apparatus

Select the gas mixture to be introduced into the manifold. Turn the appropriate control valve on the panel until a flow of gas is registered on the flow meter. Restrict one of the ports in the manifold with a cork. Flush for a minimum of 2 minutes at approximately 200 cm^3/min. Adjust the flow rate to some value at least 25 percent greater than the sampling rate of the pump which will be used to draw a sample from the manifold. The gas may now be sampled.

If samples are to be taken continuously it is not necessary to reduce the flow between samples. If, however, some time may elapse between sampling, it is advisable to reduce, or shut off, the flow to conserve the contents of the cylinder.

After completion of sampling with a mixture, the valve on the panel is closed. After the indicated flow has dropped to zero, or some insignificant value, the next sample may be introduced. The manifold should be flushed for one or two minutes at 200 cm^3/minwith each succeeding gas mixture before sampling.

D. Troubleshooting

1. Flow meter

The manual for the flow meter installed in this unit is included with the unit and includes troubleshooting information.

2. Leaking Valves

If flow is observed with a valve apparently closed, it is an indication of a leak across the valve seat.

A judgment must be made as to whether the leak is of sufficient volume to require drastic remedies. The leak may either be ignored, eliminated, or rendered harmless to subsequent samples by shutting off the line containing the leaking valve at the cylinder. The line should then be briefly opened to the manifold to reduce pressure in the line.

E. Components

1. Valves

The valves are coarse regulating valves with good shut-off features.

2. Tubing and Connections

Tubing is 1/8 in or 1/4 in o.d. by 0.032 in wall refrigeration grade copper tubing. This tubing should not be used for pressures above 1500 psi. All connections are 1/4 in or 1/8 in "Swagelok."

3. Flow meter

The flow meter is a commercial instrument which senses flow by measuring the rate of heat loss from an element exposed to the flowing gas. The flow measurement for this apparatus need not be precise but must only assure the operator that the flow into the manifold exceeds the flow out through any sampling device.

The flow meter can be removed easily for recalibration or use elsewhere. The calibration is valid for air or nitrogen but would require recalibration for gases of differing thermal conductivity.

Recalibration, if this becomes necessary, is described in the instruction manual for the flow meter.

4. Filter

The filter is a sintered metal disc capable of retaining particles greater than 50 micrometers in diameter. Particles smaller than this will not affect the flow meter.

F. Summary of Instructions

1. Attach regulator or valve to cylinder and flush with gas mixture.

2. Attach cylinder to apparatus with clean 1/8 in copper tubing.

3. Flush each line separately.

4. Check for leakage across each valve.

5. Flush manifold.

6. Adjust flow of desired mixture to appropriate value.

7. Begin sampling.

3. GAS BLENDING SYSTEM

(C_6H_6, CCl_4, C_2HCl_3, C_2Cl_4)

A. Introduction

A number of substances can be prepared as relatively concentrated mixtures in air at elevated pressure but which may not have sufficient stability to permit long term storage or use without intermittent analyses. However, if the short term stability of such mixtures is adequate, they may be used for preparing other mixtures by quantitative dilution, if some means is available for measuring the concentration relative to a reliable standard. Hydrocarbons and halogen substituted hydrocarbons, such as trichloroethylene, tetrachloroethylene, and carbon tetrachloride, give adequate and reproducible response with a flame ionization detector (FID). The flame ionization detector can be calibrated with mixtures of stable hydrocarbon mixtures such as methane or propane in air.

The system described herein produces mixtures of a gas or vapor in air at predictable and adjustable concentrations. While the system was designed primarily for the preparation of less stable gas mixtures it may be used for the preparation of a variety of binary or even multi-component gas mixtures. In such cases, the number of calibration standards required in a given situation may be minimized.

The apparatus consists of a sub-system for controlling and measuring the flow of a stream of clean and dry air and of a sub-system for introducing a gas or vapor, or a mixture of a gas or vapor in air, at a controlled rate into the air stream. The combined stream is mixed and transported to a manifold from which samples may be taken for calibration. In addition, a third sub-system is included which may be used to admit a third substance to the combined stream. The third substance may be either water vapor or a substance suspected of being an interference in the analytical system to be calibrated. It may either be admitted from a container under pressure or may be pumped in from a system at atmospheric pressure. Photographs of the gas blending unit are shown in Figures 3.1, 3.2, and 3.3. Figure 3.1 is a view of the assembled apparatus. Figure 3.2 shows details of the arrangement of components within the cabinet while Figure 3.3 shows the arrangement beneath the chassis.

B. Description of Gas Blending System

1. Components

The system is shown schematically in Figure 3.4, and consist of the following sections:

a. A sub-system (Air) for introducing air at a controlled and measured rate.

b. Two sub-systems (A, B) for introducing other gases at controlled and measured rates into the diluent air.

c. A sub-system (C) for introducing a gas from a pressure source at a measured rate.

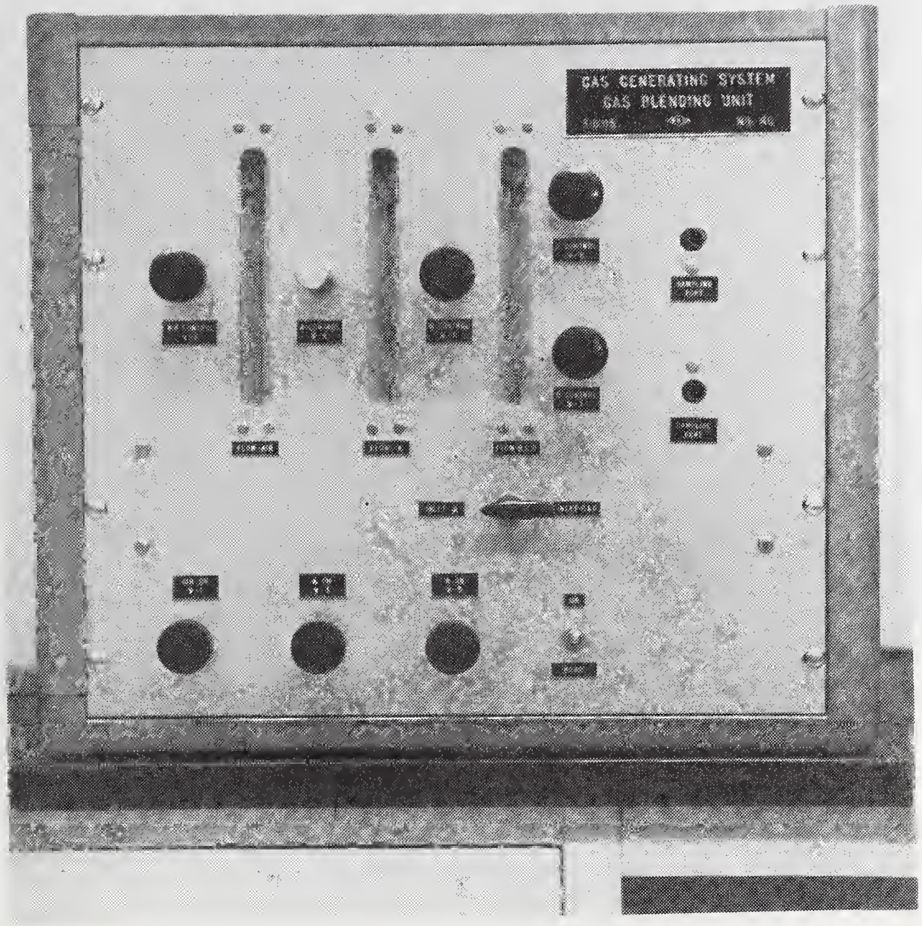

Figure 3.1 Photograph of gas blending unit

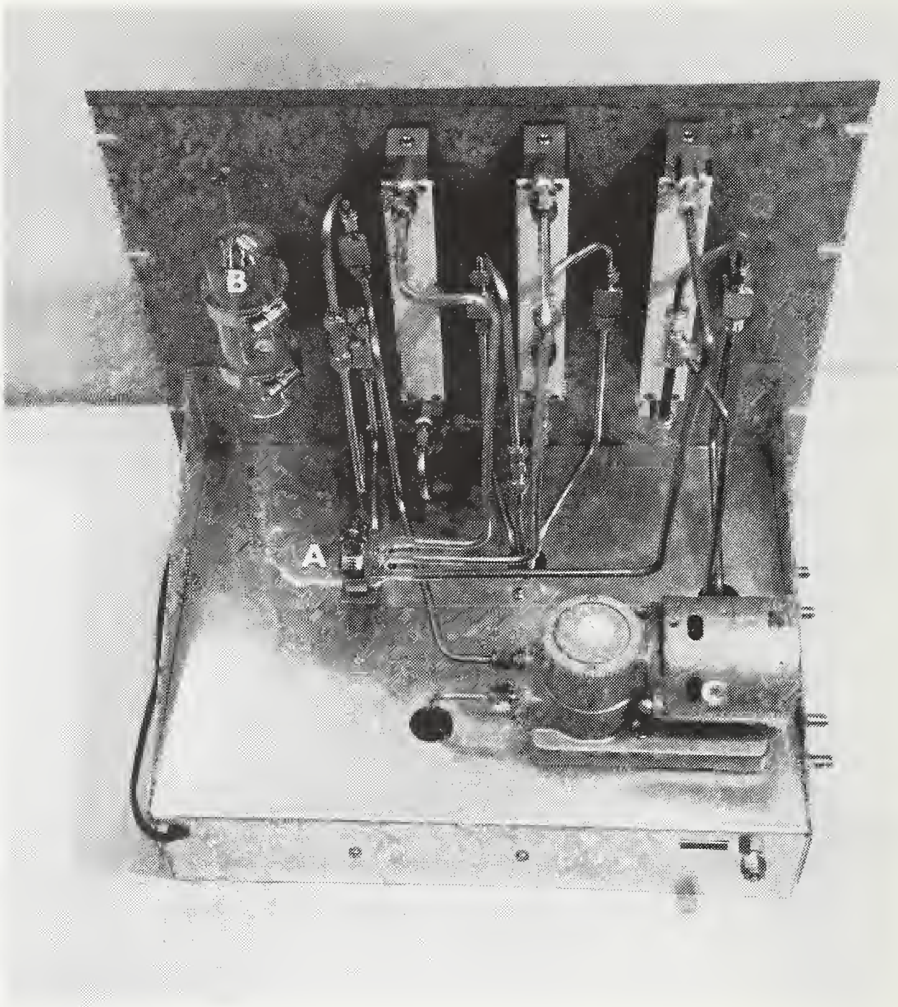

Figure 3.2 Arrangement of components inside cabinet
A. Mixing chamber B. Manifold C. Pump

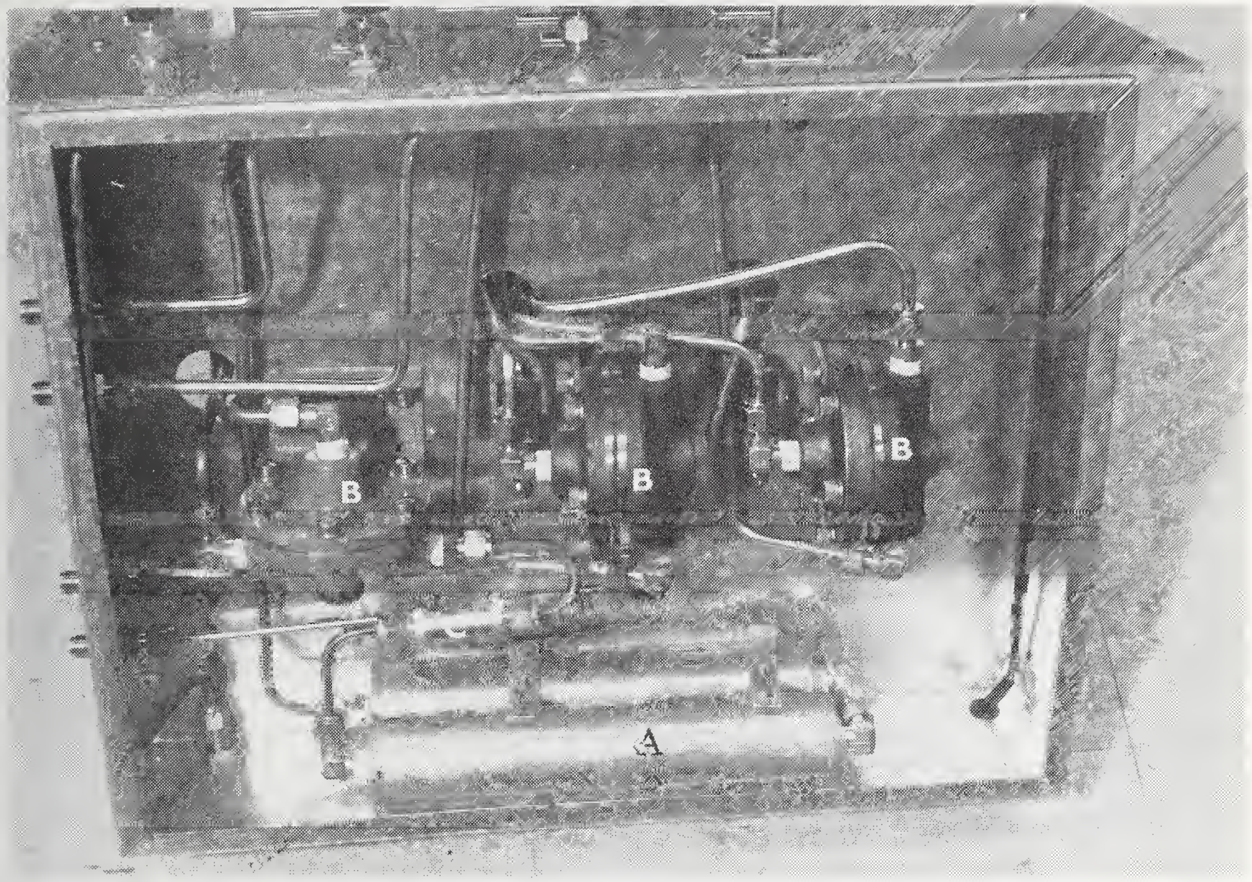

Figure 3.3 View under chassis of gas blending unit
A. Drier B. Differential flow controllers
C. Filter

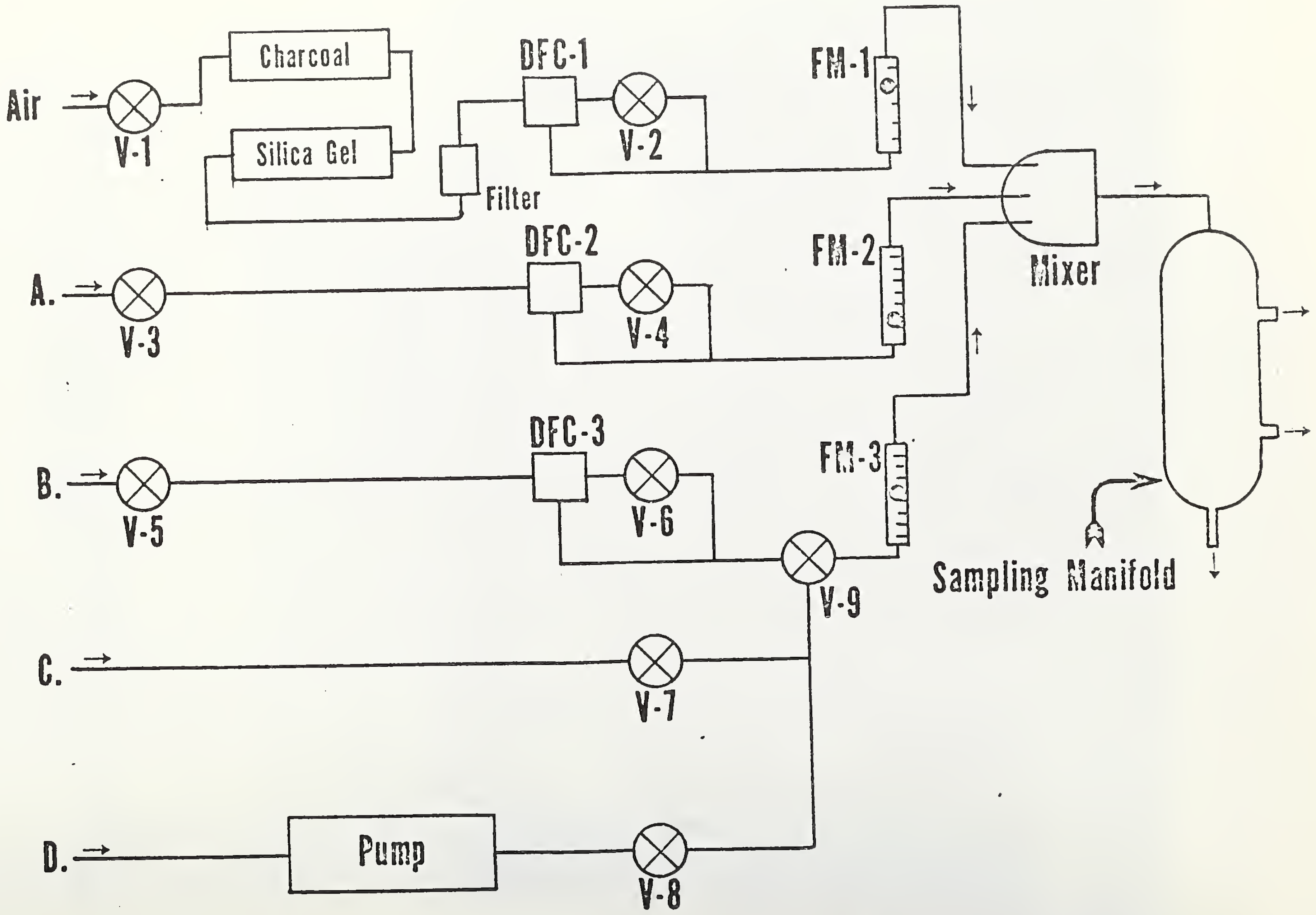

Figure 3.4 Schematic Diagram of Gas Blending System.

d. A pump (D) for introducing a gas from a source at atmospheric pressure, at a measured rate.

e. A mixing chamber for combining two or more of the above gas streams.

f. A sampling manifold from which the mixed gases may be withdrawn for analysis.

2. Diluent Air

Air at a pressure greater than 10 psi and less than 100 psi is admitted to the system at the connection marked "AIR" located at the rear of the chassis. A valve, (V-1), is provided to shut off the supply of air when the system is not in use. The air passes through two small cylinders located beneath the chassis which are filled with silica gel and charcoal. These are included to protect the system from minor quantities of water vapor and organic materials in the supply air. The supply air should be moderately clean and dry to minimize the necessity for the reconditioning of the dryer and purifier in the system. (If this is not the case, an external trapping system should be inserted between the air supply and the system.) The air then passes through a sintered metal filter into a flow control system and through a flow meter to the mixing chamber. The flow control system consists of a differential flow controller (DFC-1) and a flow control valve (V-2).

3. High Concentration Mixture

The substance to be diluted with air to produce the mixture may be introduced from a gas cylinder at the connection marked "A" or "B" located on the left side of the chassis and accessible through the slot cut into the side of the cabinet. The pressure at this inlet should be greater than 10 psi and less than 100 psi. Shut-off valves, (V-3) and (V-5), are located between the inlet connections and the rest of the system. Control of the flow is accomplished with differential flow controllers (DFC-2) and (DFC-3) and control valves (V-4) and (V-6). It should be noted that V-4 is a fine control valve and not a shut-off valve. It should never be closed more than finger tight. The flow from inlet "A" passes directly to a flowmeter and then to the mixing chamber. The flow from inlet "B" passes first through a 3-way valve, (V-9), then through a flowmeter (FM-3) to the mixing chamber.

Inlet C, passes directly through a flow control valve (V-7) to the 3-way valve (V-9). A cylinder of gas at elevated pressure may be connected to "C" and may be bled into the system but not with the same degree of control offered by A or B.

Inlet D is provided with a pump which allows gases at atmospheric pressure, for example, those generated in another system, to be introduced into the mixing chamber. The valve (V-8) and flowmeter (FM-3) are used to control and measure the quantity of gas introduced at this inlet.

The mixing chamber is designed to rapidly mix any of the streams with the air prior to passage into the manifold.

The manifold is provided with sampling ports from which samples may be withdrawn for testing or analysis. An additional outlet is provided for direct connection to an analytical instrument.

C. Operation

1. Preparation of Binary Mixtures. Connect a supply of clean and dry air to the air inlet at the rear of the chassis. Connect to inlet A a cylinder containing the desired component, either as the pure substance, or diluted to some known value considerably above the final desired concentration. Calculate the ratio of flow rates necessary to produce the desired final concentration. Consult the calibration curves accompanying FM-1 and FM-2 to determine the proper settings. Close V-2 and V-4. Open V-1 and V-3. Adjust V-2 until the proper flow is indicated by FM-1. Adjust V-4 until the proper flow is indicated by FM-2. The gas delivered to the manifold should now be of the calculated composition.

2. Analysis. The agreement between a calculated composition based on a measurement of flow rates and the actual composition produced by the unit may differ somewhat depending on a number of factors. Very high flow rates, for example, may result in back pressure in parts of the system which may then alter the composition from the predicted value. Consequently, a means of monitoring the concentration produced is desirable for producing mixtures of a moderate degree of accuracy. The mixture produced by the generating system is essentially a binary gas mixture composed of a substance in air. A flame ionization detector (FID) is an ideal analytical tool for the analysis of such systems because of the high sensitivity to compounds containing C-H bonds and because of the extreme insensitivity to the components of air. A FID is supplied with this unit and is connected to sample directly out of the manifold.

Different organic substances give different responses to equal molar quantities. Therefore, it is necessary to calibrate the FID for each substance which is to be analyzed. Four bulk gas mixtures are supplied with this unit which consist of high concentrations of benzene, carbon tetrachloride, perchloroethylene and trichloroethlene, all contained in air. The response of each of these substances relative to either methane or propane has been determined. Calibration of the FID for each substance is accomplished by determining the response of the instrument to known concentrations of either methane or propane and relating the signal observed from the other substances to the actual concentration by use of the predetermined response factors.

Attach a short length of Teflon tubing between a sampling port of the manifold, or the extra connection on the upper end of the manifold, and the FID. Consult the instruction manual accompanying the FID and prepare it for analyses. The diluent "air" is used to establish the "zero" and either propane or methane is used to establish the "span". Attach either the cylinder of methane or propane in air mixtures at C and rotate V-9 to the position marked "C or D". Adjust the span gas flow with V-7 and measure the flow with FM-3. Alternate the air and the methane or propane standard until a reproducible signal is obtained. The instrument is now direct reading for whichever hydrocarbon is used to establish the span.

Attach the bulk mixture to C and observe the signal. The signal is either the methane or propane equivalent of the concentration of the particular substance in the bulk mixture.

This signal must be multiplied by an appropriate factor to convert the observed signal, C_{obs}, to the concentration of the substance in the bulk mixture, C_x. The concentration is calculated as follows:

$$C_x = C_{obs.} \times K$$

where K is chosen for either methane or propane. The appropriate values for K are given in Table 3.1.

Table 3.1 Value of K for Calibration with Either Propane or Methane

Bulk Mixture	K_{CH_4}	$K_{C_3H_8}$
Carbon Tetrachloride	11.1	33.3
Trichloroethylene	0.562	1.69
Tetrachloroethylene	0.440	1.32
Benzene	0.204	0.611

3. Addition of Other Substances. Addition of water vapor or other substances to the binary mixture requires that the bulk mixture be attached at A. A cylinder containing the substance to be added should be prepared at an appropriate concentration determined by the nature of the experiment. Water vapor is introduced as saturated air at C from the Saturator. (Section 8.)

4. Calculations. The concentration of a substance prepared by dilution of a bulk mixture with this apparatus can be calculated as follows:

$$C_x = \frac{F_x}{F_x + F_{air}} \cdot C_b$$

where C_x = concentration produced in the manifold

F_x = measured flow rate of bulk mixture

F_{air} = measured flow rate of air

C_b = concentration of bulk mixture in ppm

The concentration of the same substance in a mixture diluted further with an interfering substance or with water vapor is calculated as follows:

$$C_x = \frac{F_x}{F_x+F_y+F_{air}} \cdot C_b$$

where F_y = measured flow rate of interfering substance or moist air.

The relative humidity of the mixture resulting from addition of moist air is calculated with the following equation:

$$Rh_2 = Rh_1 \cdot \frac{F_y}{F_x+F_y+F_{air}}$$

where Rh_2 = relative humidity of the mixture

Rh_1 = relative humidity of the moist air

F_y = measured flow rate of the moist air.

The relative humidity of the moist air, Rh_1, is calculated as described in Section 8, if the same or similar apparatus is used to produce the moist air.

D. Materials of Construction

The system is constructed of copper, brass, stainless steel, glass and Teflon. The "Air" subsystem is constructed primarily of brass and copper while the subsystems "A", "B", and "C" are constructed primarily of stainless steel wherever practical. The pump has an aluminum body and a Neoprene diaphragm.

4. OZONE SYSTEM

A. Introduction

This system produces known concentrations of ozone in a flowing air stream. The system is composed of two parts; (1) the main cabinet which houses a gas flow unit to provide a constant, known flow of air, an ozone generator and a gas manifold to sample the air stream, and (2) a separate power supply for the ozone generator. In addition, a small oxidant analyzer, a commercial microcoulomb oxidant sensor, is also supplied to continuously monitor the ozone concentration if this is desired.

B. Principle of Operation

A controlled flow of air is passed through a quartz tube which is irradiated by an ultraviolet source. The concentrations of ozone can be controlled by varying either the intensity of uv radiation reaching the quartz tube and/or by varying the flow of air through the quartz tube. A photograph of the interior of the apparatus showing the location of the principal parts is shown in Figure 4.1.

1. Gas Flow Unit

A diagram of the system is shown in Figure 4.2. Clean and dry air at a maximum pressure of 100 psi enters the system through valve V-1. The air passes successively through a column of charcoal and a column of silica gel. These serve only as a precaution to remove residual moisture and other impurities from the air supplied to the unit.

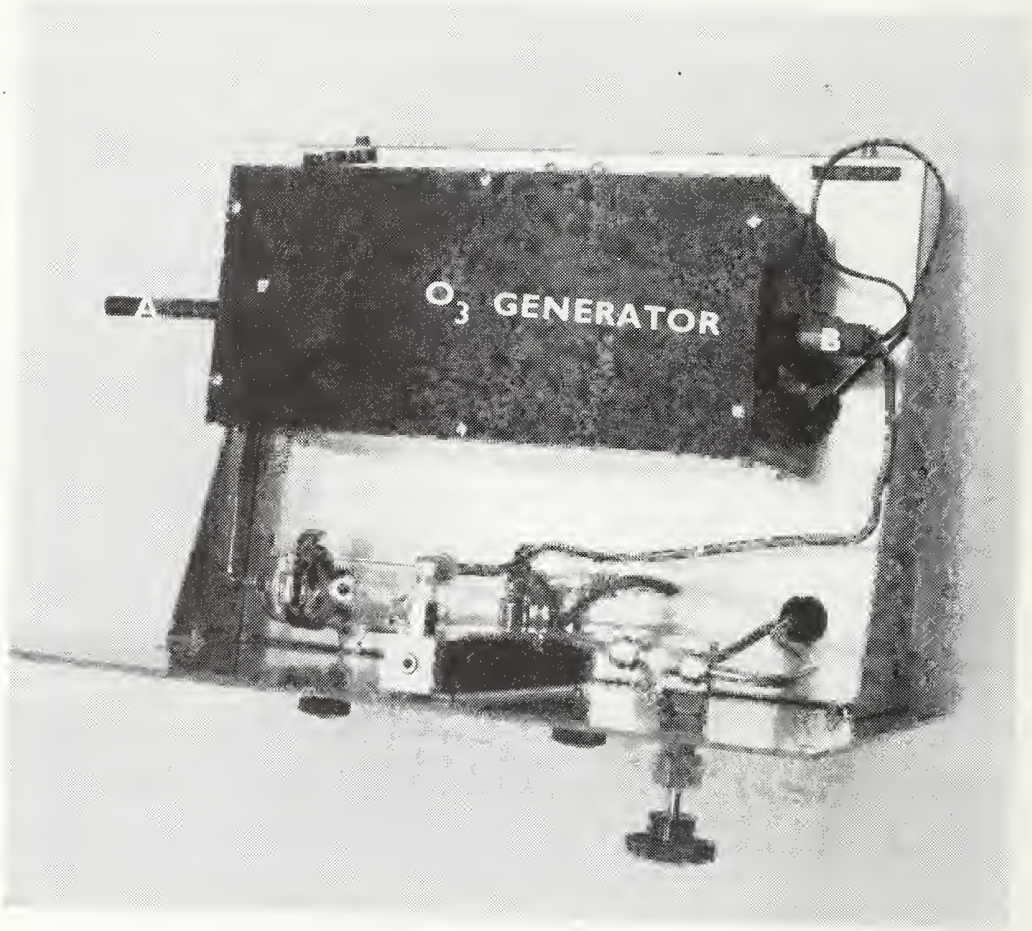

Figure 4.1 Photograph of ozone system showing location of principal parts
A. Shutter B. Lamp C. Sampling manifold

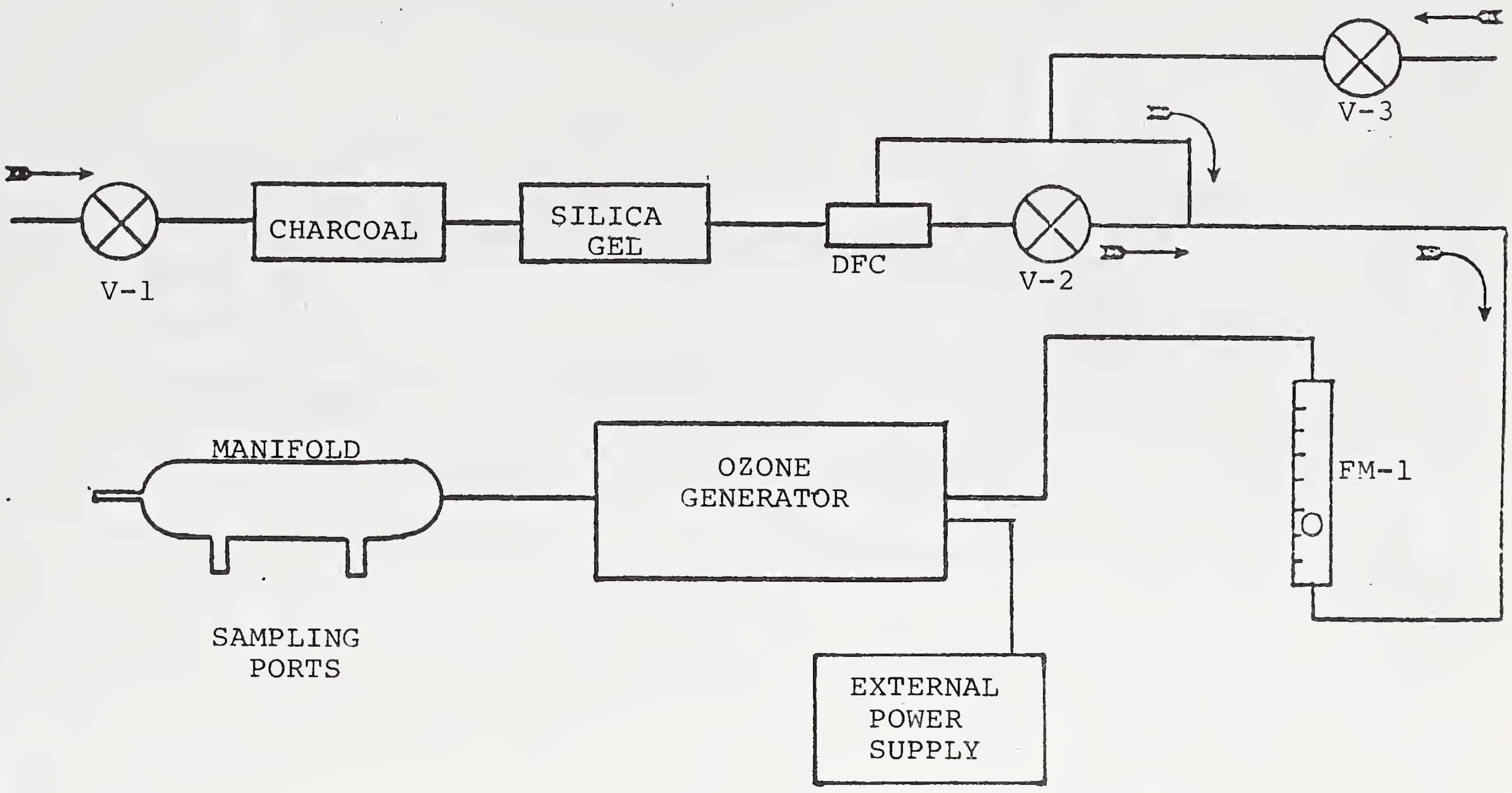

Figure 4.2 Schematic Diagram of Ozone System.

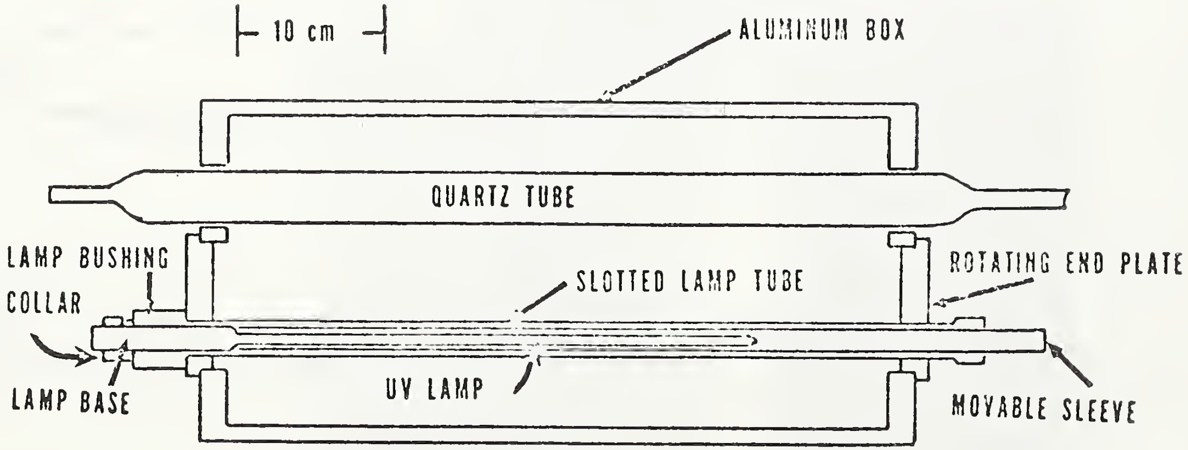

Figure 4.3 Detail of the Ozone Generator.

The flow of air through the ozone generator is controlled by V-2 . The flow is maintained at a constant value at any setting of V-2 by a differential flow control, DFC . The flow is measured with a rotameter. Valve V-3 is used in conjunction with an external supply of air of known humidity (See Section 8). Valve V-3 is normally closed except when it is necessary to operate the generator with air of known humidity. In this case, V-2 is fully closed and the flow is controlled by V-5 on the humidifier.

2. Ozone Generator and Power Supply

The ozone generator is located in the main cabinet and is operated by the separate power supply. Construction details of the generator are shown in Figure 4.3. The air stream flows through the quartz tube which extends through the length of the box. An ultraviolet mercury vapor lamp is located in a metal tube parallel to the quartz tube. A narrow slot is cut into the length of the metal tube to restrict the light impinging on the quartz tube. Ozone is produced in the air stream as it passes through the quartz tube by the reaction of the uv light with oxygen in the air. The concentration of ozone produced is varied by adjustment of a movable sleeve which slides inside the first metal tube over the lamp and which determines the amount of light that reaches the quartz tube. The sleeve is marked with a scale of one hundred equal intervals so that its position can be reproduced. The actual ozone concentrations for a given flow rate at various shutter settings are determined by chemical analysis during the initial calibration of the generator.

The separate power supply contains a constant-voltage transformer to insure a constant light intensity and a high-voltage transformer for the operation of the lamp. Three convenience outlets controlled by the main switch of the power supply are located on the back of the chassis along with two fuses. A 15A fuse protects the entire system and a 3A fuse protects the power to the transformer primary. The outlets may be used to supply power for auxillary units such as the oxidant analyzer and a recorder. A timer is included in the primary circuit of the lamp transformer which indicates the number of operational hours of the lamp.

3. Oxidant Analyzer

The oxidant analyzer, a separate commercial microcoulometric oxidant sensor, is included in the system to allow the continuous monitoring of the ozone produced in the air stream while the system is in operation. It is not intended that the analyzer be used to verify the actual concentration of ozone produced as this is determined by the shutter setting. The oxidant analyzer contains a continuous solution system to allow unattended operation for two weeks or more.

C. Operation

1. Gas Flow Unit

a. Dry Air.

1. Close all valves (V-1, V-2 and V-3)

2. Attach the air supply to the unit with stainless steel or copper tubing at the connection at the rear of the cabinet marked "Dry Air".

3. Adjust air supply pressure to a value less than 100 psi but greater than 10 psi.

4. Open V-1 (Dry Air Off) and adjust flow with V-2 (Dry Air), to the normal value of 5 l/min.

b. Humid Air. (Refer to Section 8 before proceeding.)

1. Close V-4 (On-Off) and V-5 (Control) on humidifier.

2. Turn regulator handle fully counterclockwise.

3. With 1/4 in copper tubing, attach humidifier to air supply at a pressure between 10 and 100 psi.

4. Attach humidifier to ozone generator with 1/4 in copper tubing.

5. Open V-4 slowly with V-5 closed.

6. Select desired relative humidity and adjust regulator to obtain pressure shown below:

Relative Humidity in Percent	Pressure Psig
100	0
75	5
50	15
33	45
25	60

7. With V-3 fully opened and V-2 fully closed flow is adjusted with V-5 on the humidifier to the normal value of 5 l/min as indicated by the rotameter on the ozone generator cabinet. The rotameter on the humidifier should not be used to measure flow for the ozone generating system.

2. Ozone Generator

The ozone generator is operated in the following manner:

a. Attach lamp cord to the power supply.

b. Turn on the main power supply switch, which is the upper switch on the power supply cabinet.

c. Turn on the switch for the uv lamp which is the lower switch on the power supply cabinet.

d. Line up the mark on the shutter tube which corresponds to the desired concentration of ozone with the end of the outer brass tube.

The shutter setting for the desired concentration of ozone is obtained from the calibration curve of shutter setting *vs* ppm of ozone, Figure 4.4. This calibration curve is valid only for a flow rate of 5 l/min corresponding to a rotameter reading of 68.0 for the top of the stainless steel float. If other flow rates are used a recalculation of the ozone produced must be made based on the new flow rate. The lamp of the ozone generator should be turned on several hours before use to obtain a stable ozone output. To avoid accumulation of ozone in the atmosphere in the vicinity of the unit it is recommended that the shutter tube be in the zero position during warm-up periods and at any other time when the system is left on but is not in use. The ozone concentration produced by the generator stabilizes within seconds after the shutter setting is changed. The oxidant analyzer, however, may require a considerably longer time to re-establish equilibrium.

3. Oxidant Analyzer

Detailed instructions for the operation of the analyzer are given in the manufacturer's instruction manual, which should be consulted before use. It should be noted that the analyzer is turned on 24 hours before use. The analyzer may be plugged into one of the convenience outlets on the back of the power supply which are activated by the main power switch. If the system is to be used over an extended period of time

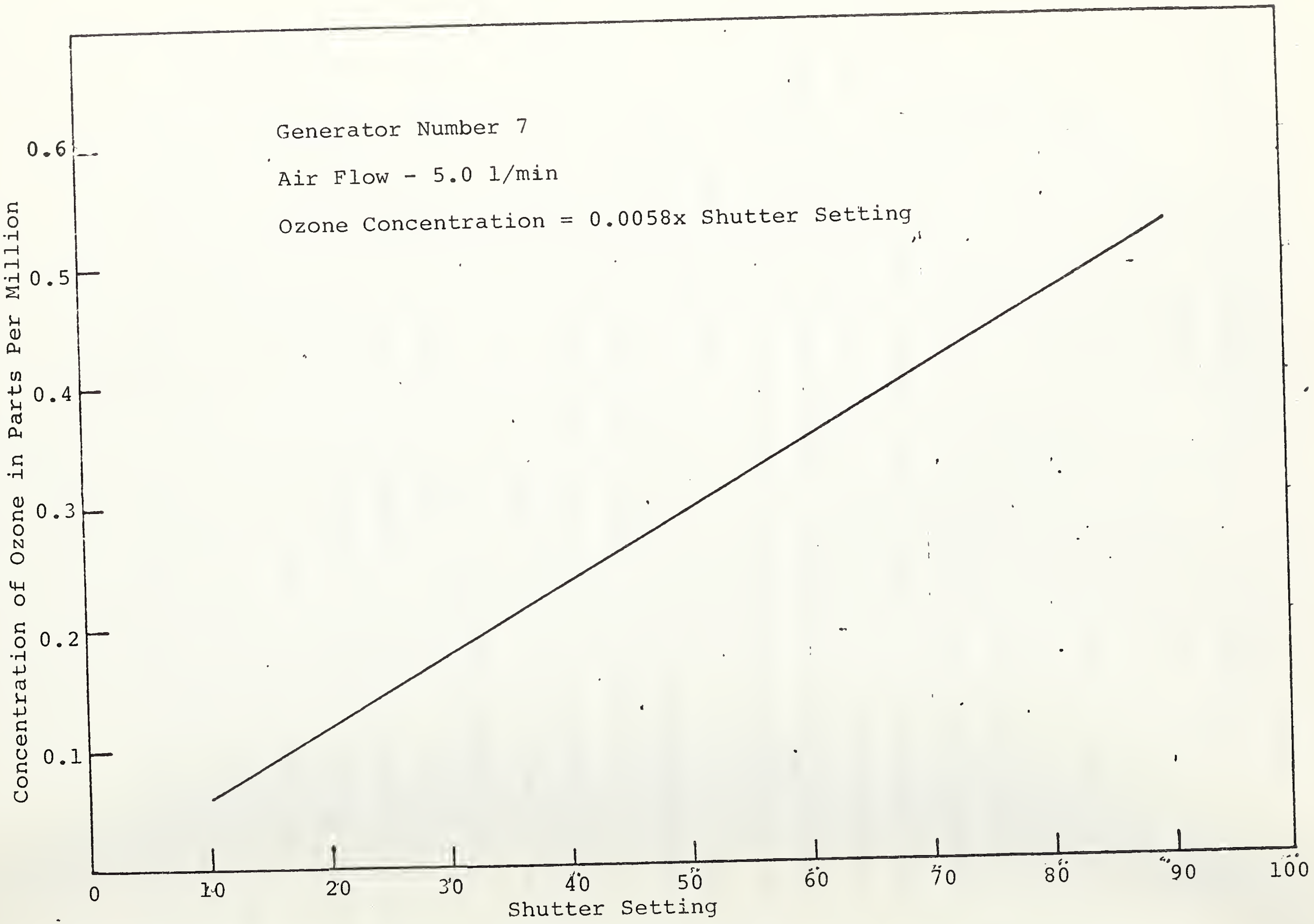

Figure 4.4 Calibration of Ozone Generator Number 7.

the analyzer should be left on even while the ozone generator is turned off.

The air stream is sampled by the analyzer using a length of Teflon tubing inserted into the top of the manifold inside the cabinet.

4. Shut-Down

Complete shut-down requires that V-1, V-5 and the main power switch on the electrical cabinet must be shut off. Because the system requires a period of several hours to reach equilibrium it may be advisable at times to shut off only the air supply leaving the generator and oxidant analyzer turned on. The generator shutter should be placed in the fully closed position to prevent production of ozone in the area.

D. Maintenance

1. Gas Flow Unit

a. The drying cylinders, located underneath the main cabinet chassis, occasionally require reactivation depending upon the purity and/or dryness of the air supply. The panel with the chassis attached can be removed from the cabinet by removing the eight screws on the two edges of the panel. Tubing is removed from one end of the driers leaving them attached with the short loop of copper tubing at the other end. Heating for about one hour at 110°C while continuously flushing with dry air is sufficient to regenerate the adsorbants. After cooling, replace the cylinders in the chassis and the chassis and panel in the cabinet.

b. The rest of the gas flow unit should require no maintenance, other than replacement of components which fail in service.

2. Ozone Generator

The uv lamp ages with use and the ozone output may decline. Therefore, the ozone generator should be recalibrated after 1000 hours of use as indicated by the elapsed time meter on the power supply cabinet, or at least once a year.

3. Oxidant Analyzer

Instructions for the maintenance of the analyzer are included in the manufacturer's instruction manual. Since the analyzer supplied with this system includes a continuous solution system, the reagent solution needs to be changed only every sixty days. Distilled water should be added to the solution reservoir every two weeks to compensate for evaporation.

E. Calibration of the Ozone Generator

The primary calibration of the ozone generator is given by Figure 4.4. The calibration curve for shutter setting *vs* ppm of ozone has been determined by the neutral potassium iodide method. The generator may be returned to the National Bureau of Standards whenever recalibration is required or the recalibration may be performed by a competent chemist using the procedure outlined in "Tentative Method for the Manual Analysis of Oxidizing Substances in the Atmosphere" which appeared in Health Laboratory Sciences, Volume 7, page 152 (1970).

F. Materials of Construction

The airflow system upstream of the generator is constructed of copper and brass. The short line between the irradiation tube and the sampling manifold is glass. The irradiation tube is quartz.

5. PERMEATION TUBE SYSTEM

(SO_2, H_2S, NO_2)

A. Introduction

Permeation tubes are devices which are partially filled with a volatile liquid, often at elevated pressures, which escapes through the walls of the tube at a predictable rate. The tubes are generally constructed of Teflon, although other porous plastics may be used. At constant temperature, the material in the tube will effuse through the walls at a constant rate. The rate may be determined by weighing the tube periodically while it is held at constant temperature. The weight loss per unit time can then be calculated.

If a permeation tube is placed in a stream of air flowing at a constant rate, then a constant concentration of the material effusing from the tube will be produced in the air stream. The concentration in the air stream may be easily changed by varying either the rate of flow of the air or by changing the temperature of the permeation tube. The apparatus described herein maintains permeation tubes at a known temperature and provides a variable and measured flow of air.

B. Description of System

1. General Description

A photograph of the unit is shown in Figure 5.1. Figure 5.2 is the interior of the unit showing the location of the principal parts including the tube conditioner. A diagram of

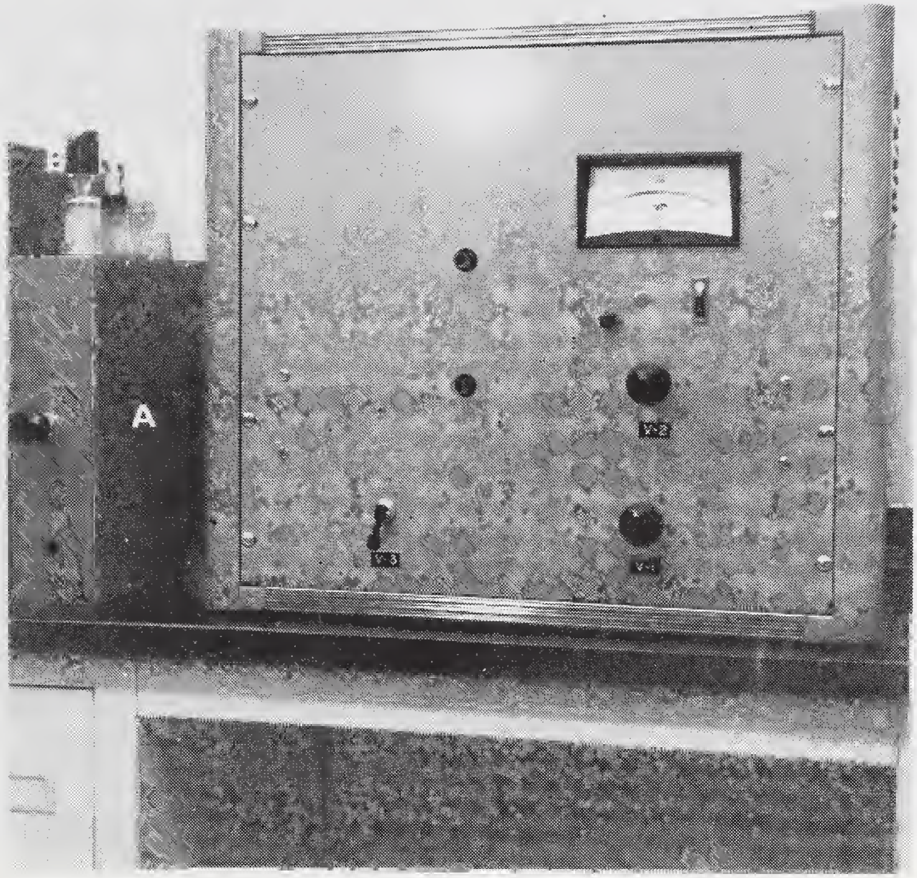

Figure 5.1 Photograph of permeation tube apparatus and tube conditioner
A. Tube conditioner B. Charcoal trap on tube conditioner

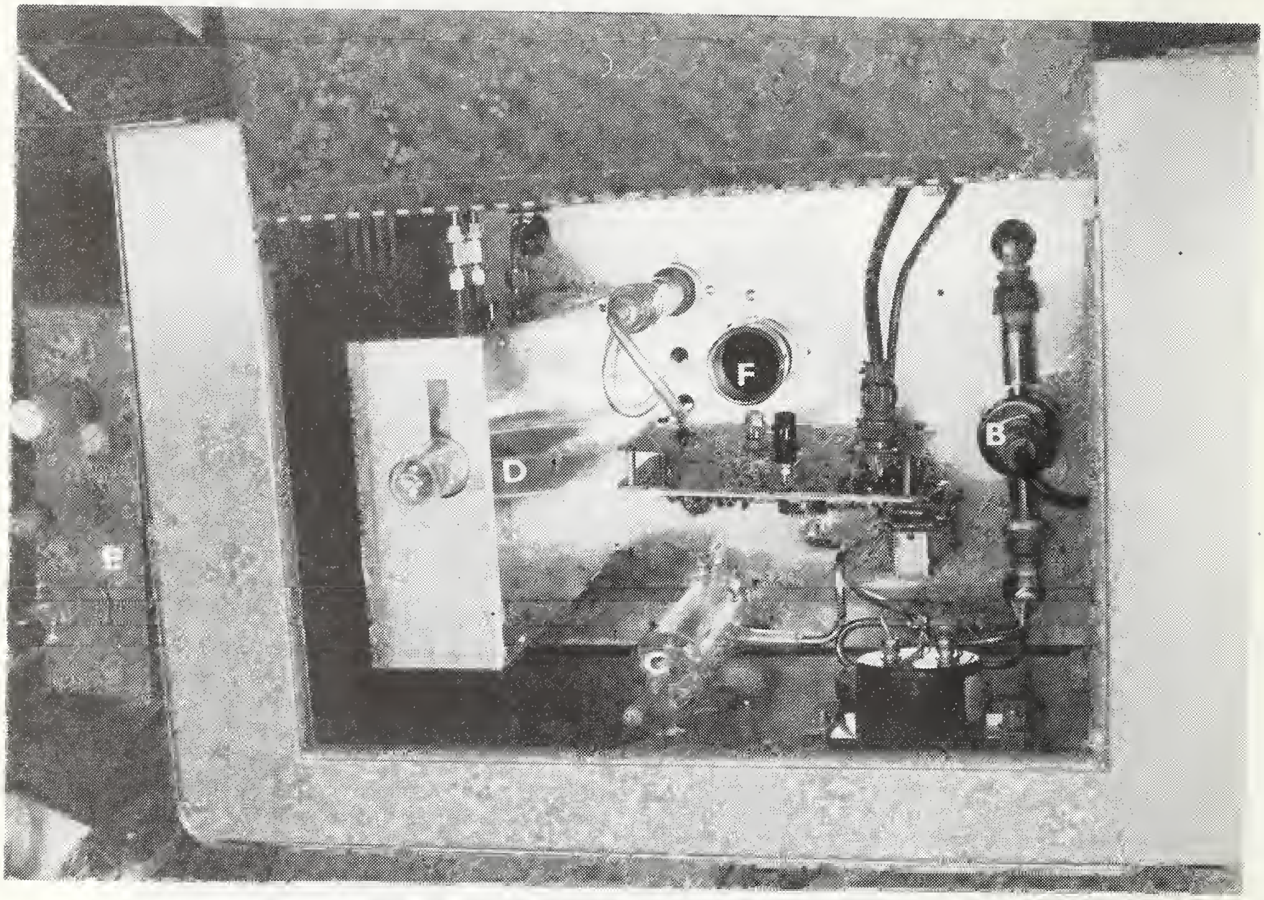

Figure 5.2 Interior view of permeation tube apparatus

A. Saturator B. Flow meter sensor head
C. Manifold D. Enclosure for exposure chamber and preconditioner E. Tube conditioner
F. Charcoal trap

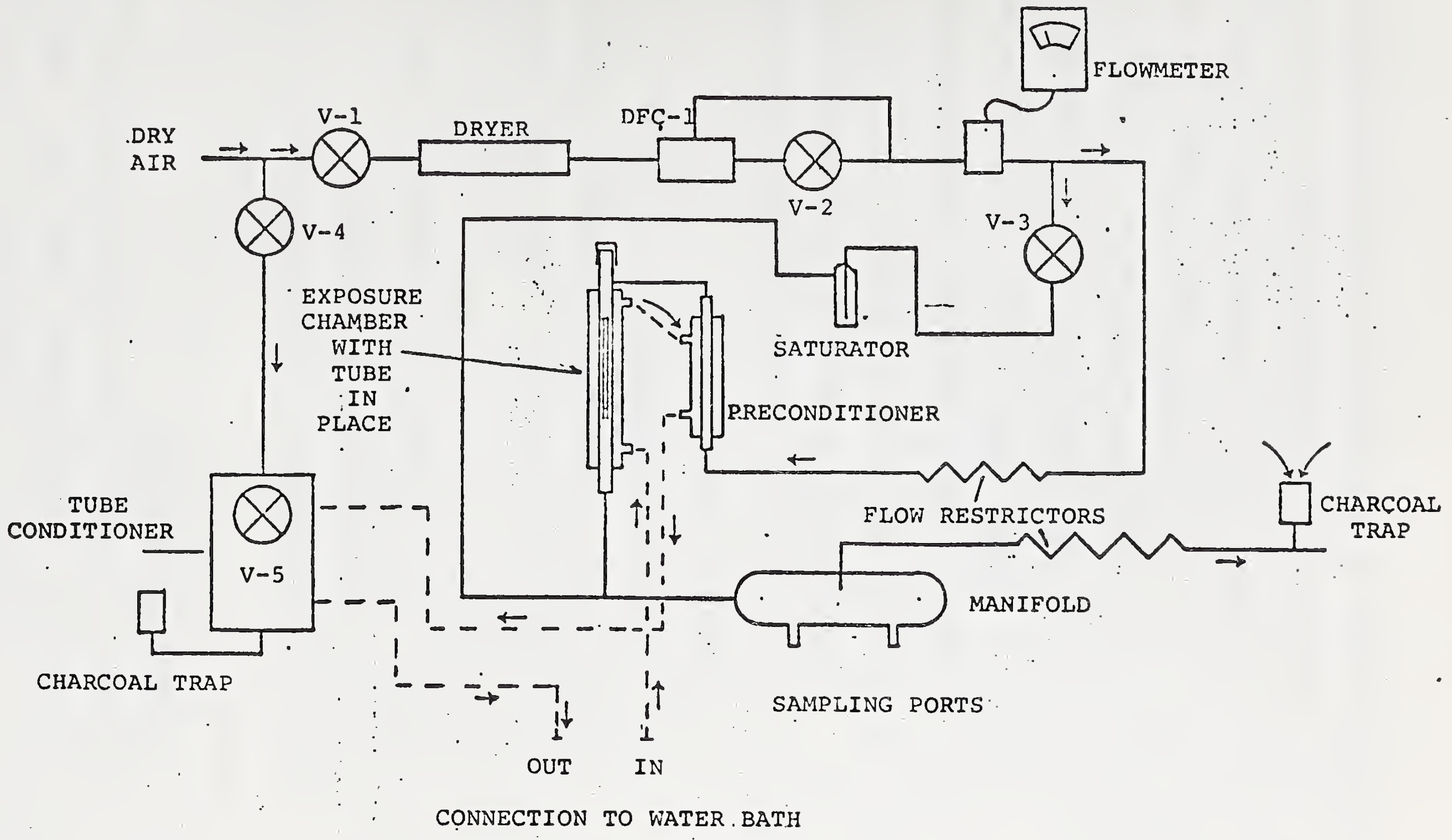

Figure 5.3 Schematic diagram of permeation tube system

the system is shown in Figure 5.3. The system includes a trap packed with charcoal and silica gel (Dryer), a flow regulating device (DFC-1), a flow meter, a water jacketed preconditioner for the supply air, a water jacketed exposure chamber for the permeation tube and a sampling manifold. An external circulating water bath controls the temperature of the exposure chamber.

An auxiliary system allows a fixed portion of the main air stream to pass through a saturator, bypassing the tube exposure chamber and recombining with the main stream prior to passage into the mixing manifold. This allows humidification of the gas in the manifold without passing humid air over the permeation tube.

A second auxiliary system allows a sample to be drawn from the manifold and to be mixed in a fixed proportion with air drawn through a charcoal trap. This reduces the concentration of any substance drawn from the manifold by a fixed amount, allowing use of analytical instruments whose range would be exceeded by the undiluted sample.

The flow restrictions are short lengths of 1/8 in stainless steel tubing.

2. Temperature Control

The permeation rate of the tube is determined by the temperature of the air passing over the tube. The temperature of the air is determined by the temperature of the water circulating through the exposure chamber and the preconditioner. Tubes are best used at or near the calibration temperature.

The temperature of the room and that of the tube should not differ by more than 5°C. The circulation rate of the water is such that the exposure chamber should be within ±0.1°C of the temperature indicated at the circulating water bath if room and bath do not differ by more than 5°C. Temperature in the exposure chamber may be measured by inserting a thermometer into the chamber and allowing it to reach equilibrium with the air stream. The top of the exposure chamber should be plugged during this operation to prevent circulation of room air into the chamber which may result in erroneous temperature readings. This is easily accomplished by using a cork drilled to fit the thermometer. During normal use of the unit a glass cap serves to close the upper end of the chamber and there is no danger of room air entering. The circulating bath should be set at the calibration temperature and after equilibrium has been reached, the temperature of the chamber is measured. If there is a difference of greater than ±0.1°C the lines between the bath and the unit should be shortened or insulated. The bath provided with the apparatus is described in detail in a manual accompanying the bath.

3. Air Flow Control

The air flow system is shown in detail in Figure 5.3. Air which has been previously dried and freed of organic vapors is brought into the system through the bulkhead connection marked "Air" at the rear of the chassis. A minimum pressure of 10 psi is required. Maximum pressures should not exceed 100 psi. Valve V-1 controls the flow of air into the system and serves to isolate the system when it is not in use. The air then passes through a cylinder packed with layers of silica gel and activated charcoal. The purpose of these is to provide assurance that the air passing through the instrument is dry and free of hydrocarbons. Valve (V-2) controls the flow through the system. The system incorporates a constant flow device so that once a flow is set, it will remain constant until the valve is again adjusted. The flow rate is indicated on a mass flow meter. The scale is marked in standard cubic centimeters per minute (cm^3/min). "Standard" conditions are defined here as 20 °C and a pressure of 760 mm. Variations in pressure and temperature of the air in the system do not affect the indicated reading. In all calculation the volume of air will be that volume indicated by the meter at the defined standard condition. Details of operation and adjustment can be found in the manual provided with the flow meter.

4. Tube Storage Device

A period of time is required for permeation tubes stored at one temperature to reach equilibrium at a different temperature. Further, tubes should never be exposed to the atmosphere other than during the brief time required to transfer a tube from storage to exposure chamber and back. A device is included in the system which allows tubes to be stored at approximately the same temperature as the exposure chamber. This is accomplished by circulating the water from the exposure chamber through the tube conditioning device before

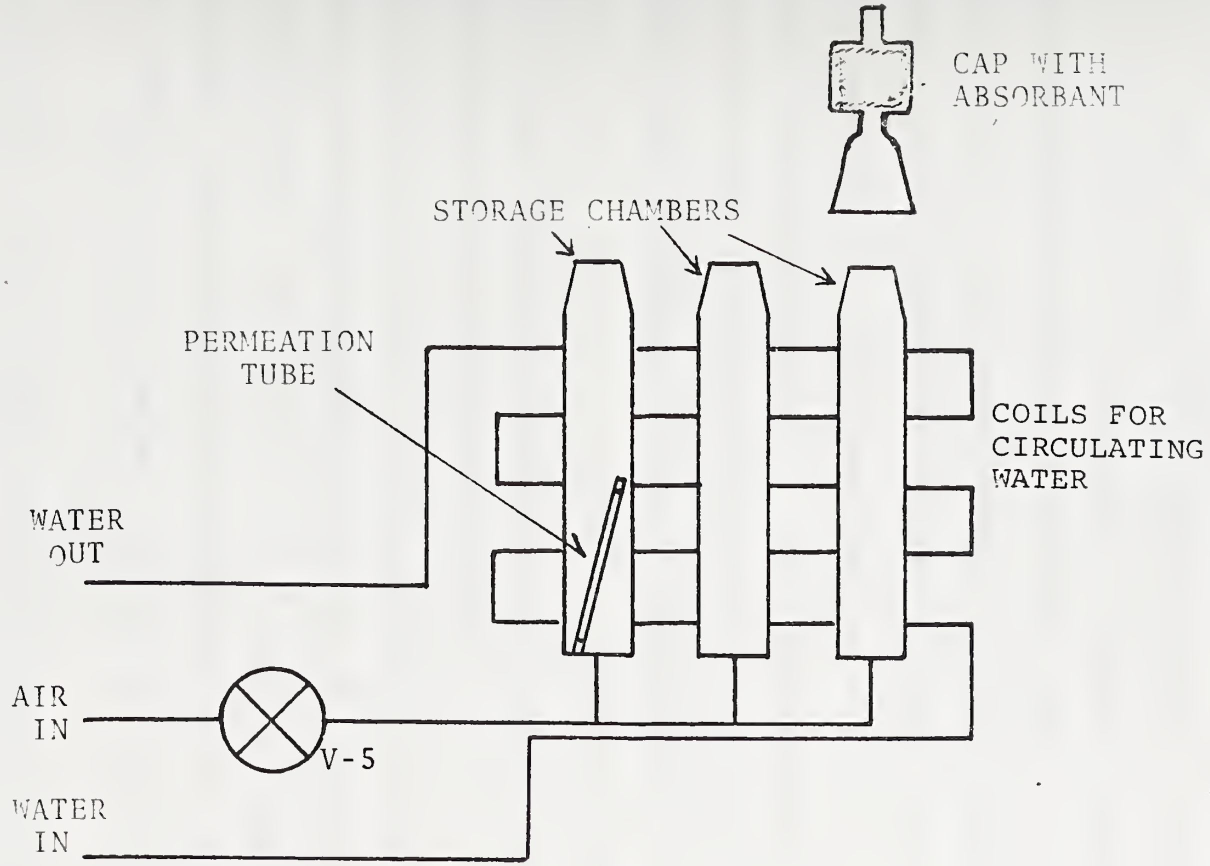

Figure 5.4 Tube Storage Device.

returning it to the water bath. A slow flow of clean air, from the same source of supply as the exposure chamber, is flushed through the tube conditioning device to remove effused material from the device. The device shown in Figure 5.4 has three separate chambers in which either three different kinds of tubes can be stored or where tubes of the same type can be stored separately. Valve V-4 is mounted external to both systems and is used to close off air flow to the storage device when it is not in use. Valve V-5 is used to control the flow through the chambers of the storage device. The tubes carrying the air and the return water are thermally connected to assure that the tubes are subjected to temperature conditions almost identical to those in the exposure chamber.

The storage device will be most often employed when it is necessary to use several tubes of different lengths and in various combinations to produce a range of concentrations. When tubes are not in the exposure chamber they are kept in the storage device ready for immediate use. Each chamber is equipped with a flow-through cap in which a small amount of activated charcoal is placed to adsorb material effused from the tube.

This device should never be used to store tubes for long periods of time. When tubes will not be needed within a day or two they should be placed in a sealed container together with a small amount of silica gel and activated charcoal and stored in a refrigerator or a freezer.

C. Use of Apparatus

1. General Instructions

A source of dry, clean air at a pressure between 10 and 100 psig is connected to the single bulkhead connector at rear of chassis, marked "Air". A short length of Tygon tubing is connected between outlet of circulating pump on temperature control bath and upper connection of exposure chamber. This connection is accessible through the holes in the door at the rear of the cabinet. The tube storage device is positioned close to the main cabinet and a piece of Tygon tubing is connected between the lower hose connection on the exposure chamber and one of the hose nipples on the storage device. Another length of tubing is used to connect between the other hose nipple and the inlet of the circulating pump. The bath is filled, turned on, and adjusted to the desired temperature.

A supply of air from the same source as is used to feed the main instrument is connected to the bulkhead connection of the storage device using an external shut off valve V-4. A flow meter is connected to the outlet of one chamber while the other two chambers are plugged. The valve V-4 is opened until a flow of 100-500 cm^3/min is observed.

The power switch to the flow meter on the front panel is turned on. Twenty minutes is needed for complete warmup and, if necessary, adjust the zero according to manufacturer's instructions at this time.

Valve V-1 is opened fully, and then V-2 is slowly opened until a deflection of the flow meter is noted. Allow the systems to flush for several minutes. Permeation tubes of proper length are placed either in the exposure chamber or in the storage device. Tubes which have been stored at low temperature should be placed in the system at least 16 hours before use. Equilibration for shorter periods of time may result in a concentration as much as 10 percent lower than calculated.

2. Sulfur Dioxide Generation

a. Permeation Tubes. Sulfur dioxide permeation tubes furnished with this apparatus are National Bureau of Standards, Standard Reference Materials, and have been individually calibrated over a temperature range from 20 to 30 °C. The nominal rate for this type of tube is 0.4 μg/min per cm of tube length at a temperature of 30 °C. Table 5.1 is a guideline to the number and length of tubes needed to produce the indicated concentration at the indicated flow rate. Minor adjustment of the flow rate will be needed to compensate for actual permeation rates which are given in the SRM certificate.

Table 5.1 Flow Rate, Tube Length, and Concentration Produced, for Sulfur Dioxide Permeation Tubes at 30 °C

Concentration, ppm	Tube Length, cm	Flow Rate, ℓ/min
2.5	10	0.625
5.0	20	0.625
10.0	40	0.625
25.0	40	0.250

The permeation rate in micrograms per minute, G, the rate of air flow in liters per minute, F, and the concentrations of sulfur dioxide in the air stream, C, are related as follows:

$$C = \frac{G}{F} \cdot K$$

The values of K at various temperatures may be found in Table 5.4. The equation can be used to calculate the required volume flow to produce a fixed composition for any sulfur dioxide permeation tube or combination of tubes.

When the required tubes and the flow rates have been selected, the tubes are hung in the chamber and the flow is carefully adjusted to the required value.

b. Analytical System. A flame photometric sulfur analyzer is provided to monitor the sulfur dioxide in the generated atmosphere. This instrument will indicate the satisfactory functioning of the total system, but is not intended to provide the absolute measure of the sulfur dioxide concentration. This value is determined by the permeation tubes, which are the primary standards.

The instrument responds only to sulfur atoms and does not distinguish between different sulfur containing compounds. This, however, is not a disadvantage since equimolar amounts of hydrogen sulfide and sulfur dioxide give equal response. Consequently, a calibrated sulfur dioxide permeation tube may be used to calibrate the system either for sulfur dioxide or hydrogen sulfide. An instruction manual accompanies the sulfur analyzer and should be consulted for operational instructions.

The upper concentration range of the sulfur analyzer is not adequate for the high concentration produced by the generator and it is necessary to dilute the sample. Gas from the manifold is drawn at a slow rate through a short length of small diameter tubing. A larger amount of room air is then drawn into the system through a short length of activated charcoal. The moving force for the two gas streams in this part of the system is the pump attached to the sulfur analyzer. The two streams are joined and the sulfur dioxide is diluted by the ratio of the flows of the two gas streams. It is not necessary to know or measure the ratio of the two air streams as long as they remain constant relative to each other.

3. Hydrogen Sulfide Generation

a. Permeation Tube. Atmospheres containing hydrogen sulfide are produced with permeation tubes which, however, are not primary standards. However, the approximate permeation rate for these tubes is known and is used to set up the systems. The actual concentration is determined by measurement of the signal due to sulfur with the flame photometric sulfur analyzer which in turn will have been calibrated with an NBS Standard Reference Sulfur Dioxide Permeation Tube.

The approximate concentrations produced by hydrogen sulfide tubes of different lengths and nominal rate at 30°C of 0.4 μg/min per cm of length below are shown in Table 5.2.

Table 5.2 Flow Rate, Tube Length, and Concentration Produced for Hydrogen Sulfide Permeation Tubes at 30°C

Concentration, ppm	Tube Length, cm	Flow Rate ℓ/min
5	10	0.625
10	20	0.625
20	40	0.625
50	40	0.250

The same relationship described for sulfur dioxide exists between flow, permeation rate and concentration except that the constant is different as shown in Table 5.4.

All other operational features are the same for sulfur dioxide.

b. Analytical System. A calibration curve is furnished with the sulfur analyzer which will serve as a guide to the calibration of the instrument. A check of this calibration curve or preparation of a revised calibration should be made before beginning the generation of mixtures of hydrogen sulfide.

Sulfur dioxide tubes are selected to give maximum output and the flow rate is reduced to give a calculated concentration between 40 and 50 ppm. The flow from the generator manifold through the dilution apparatus is adjusted until a signal is obtained with the sulfur analyzer which is less than 10^{-5} A This value, taken as an upper limit, places the calibration points on a more linear portion of the log-log calibration curve of the instrument. After a stable signal is obtained, the flow over the tube is increased. The indicated concentration will be reduced by a factor dependent on the ratio of the original flow to this succeeding flow rate. This procedure is repeated up to maximum flow through the generator. A calibration curve can now be prepared from these points.

If no adjustment is made to the dilution apparatus, and if the sulfur analyzer is adjusted in the same manner each time, then it will not be necessary to redraw the calibration curve, but merely to confirm the previous curve.

Hydrogen sulfide tubes may now be substituted for the sulfur dioxide tubes and the flow rates adjusted to give the desired concentration. Since the instrument measures total sulfur a part per million of sulfur dioxide is equal to a part per million of hydrogen sulfide when expressed on a volume or molar basis.

4. Nitrogen Dioxide Generation

a. **Permeation Tubes.** Nitrogen dioxide permeation tubes serve both as standards and as the means of generating atmospheres of known nitrogen dioxide. While nitrogen dioxide permeation tubes will not be NBS Standard Reference Materials, they will have been calibrated by NBS and can be considered absolute within the time limits shown on the data sheet accompanying each tube or group of tubes. Nitrogen dioxide permeation tubes are available commercially with rates at 25° of about 1.0 μg/min per centimeter of length. The combination of tube lengths and the flow rates necessary for the production of concentrations of nitrogen dioxide are given in the table below.

Table 5.3 Flow Rate, Tube Length, and Concentration Produced for Nitrogen Dioxide Permeation Tubes at 25 °C

Concentration, ppm	Tube Length, cm	Flow Rate, ℓ/min
2.5	5	1.06
5.0	5	0.53
10.0	10	0.53
25.0	15	0.32

The relationship between concentration, permeation rate and air flow is the same as for sulfur dioxide and hydrogen sulfide with the appropriate constant given in Table 5.4.

b. Analytical System

The oxidant analyzer used to monitor the ozone output of the ozone generator may be used to monitor the nitrogen dioxide produced with the permeation tube apparatus. The inlet line of the oxidant analyzer is placed into the manifold through one of the sampling ports. The signal from the analyzer should be used to verify changes in concentration which result when the flow rate or number of tubes is changed but is not used to determine the absolute concentration of nitrogen dioxide. This value is determined from the measured flow rates and permeation rate of the tube.

Table 5.4 Value of K for Sulfur Dioxide, Hydrogen Sulfide and Nitrogen Dioxide at Various Temperatures

	Value of K		
Substance	20 °C	25 °C	30 °C
Sulfur Dioxide	0.375	0.382	0.389
Hydrogen Sulfide	0.708	0.720	0.732
Nitrogen Dioxide	0.523	0.532	0.541

D. Materials of Construction

Parts of the system that are exposed to the gas mixture beyond the permeation tube chamber are constructed of glass, Teflon, and stainless steel. The system upstream of the permeation tube chamber is constructed primarily of copper and brass.

6. AMMONIA SYSTEM

A. Introduction

This system produces mixtures of ammonia in air over a wide concentration range. The system consists of two units; a gas mixing unit and an analytical unit. The gas mixing unit produces low concentrations of ammonia by combining a relatively high concentration of ammonia-in-air (*i.e.* the bulk mixture) with a stream of clean, ammonia-free air, (*i.e.* the diluent). The analytical unit consists of a system which directs the bulk mixture through an impinger where the ammonia concentration is determined by titration of an acid solution of known strength. Analysis of the bulk mixture prior to use serves to confirm that the mixture has not deteriorated between analyses or serves to assess the extent of deterioration.

B. Principle of Operation

The gas mixing unit and the analytical unit are combined in one system. A photograph of the system is shown in Figure 6.1. Figures 6.2 and 6.3 show the interior of the unit and the arrangement of components beneath the chassis. The gas cylinder containing the bulk mixture is connected to the bulkhead connector on the front panel marked "Ammonia Inlet." The diluent air is connected at the rear of the chassis at the connector marked "Air In." The bulk mixture and the diluent air are mixed in known proportions and are directed to the

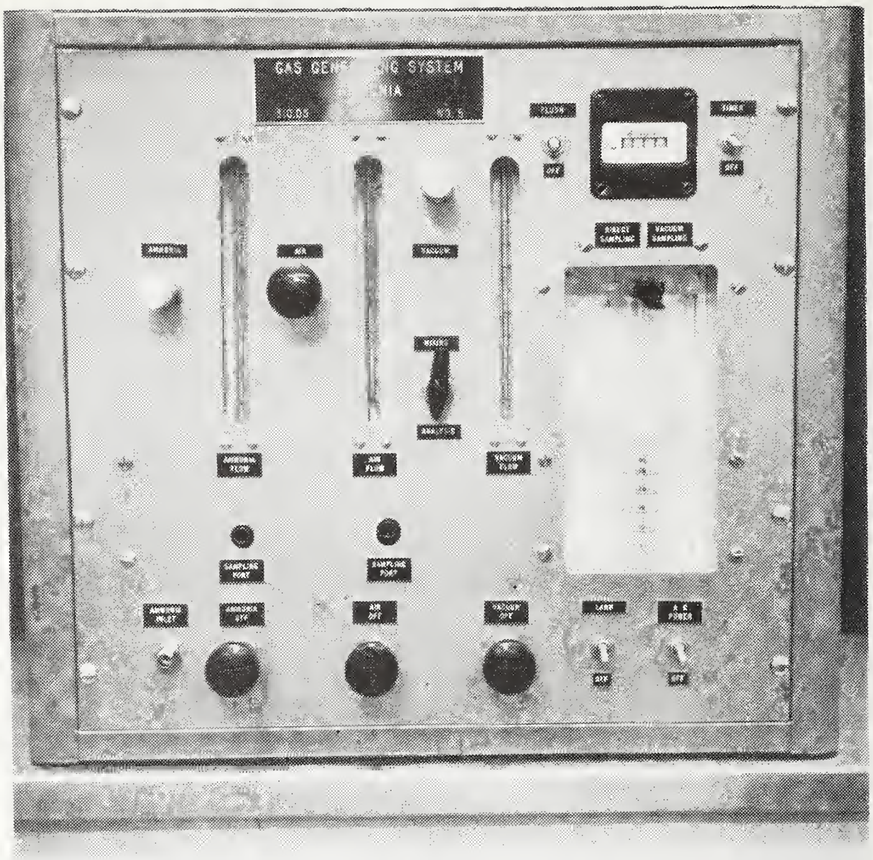

Figure 6.1 Photograph of ammonia system

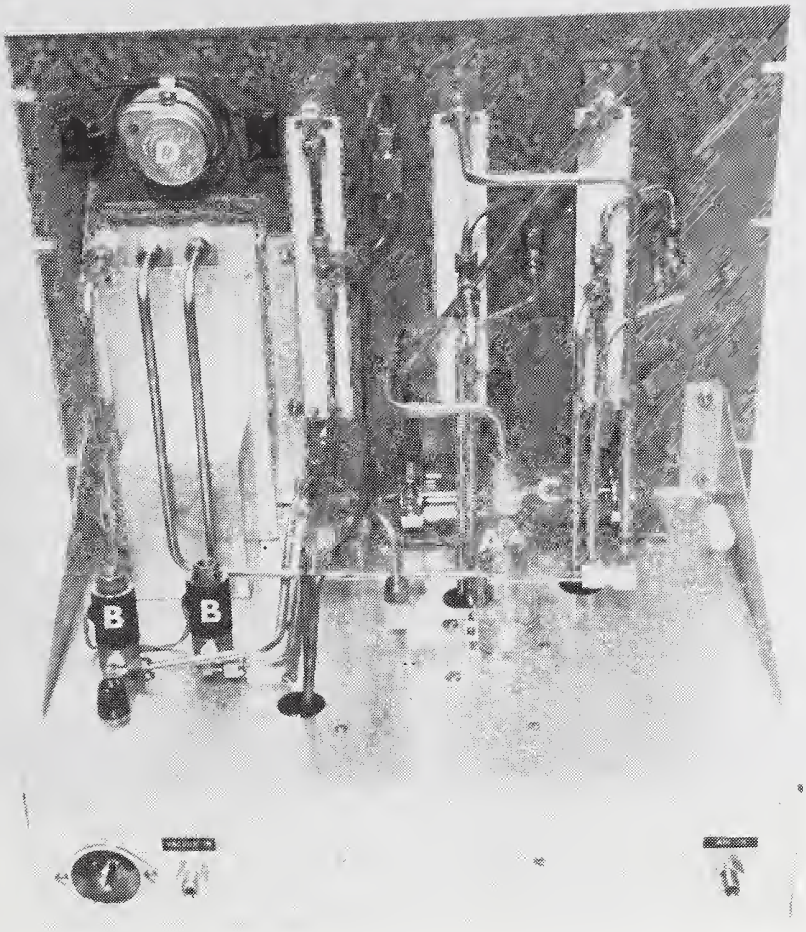

Figure 6.2 Interior view of ammonia system

A. Mixing chamber B. Solenoid valves
C. Manifold D. Timer

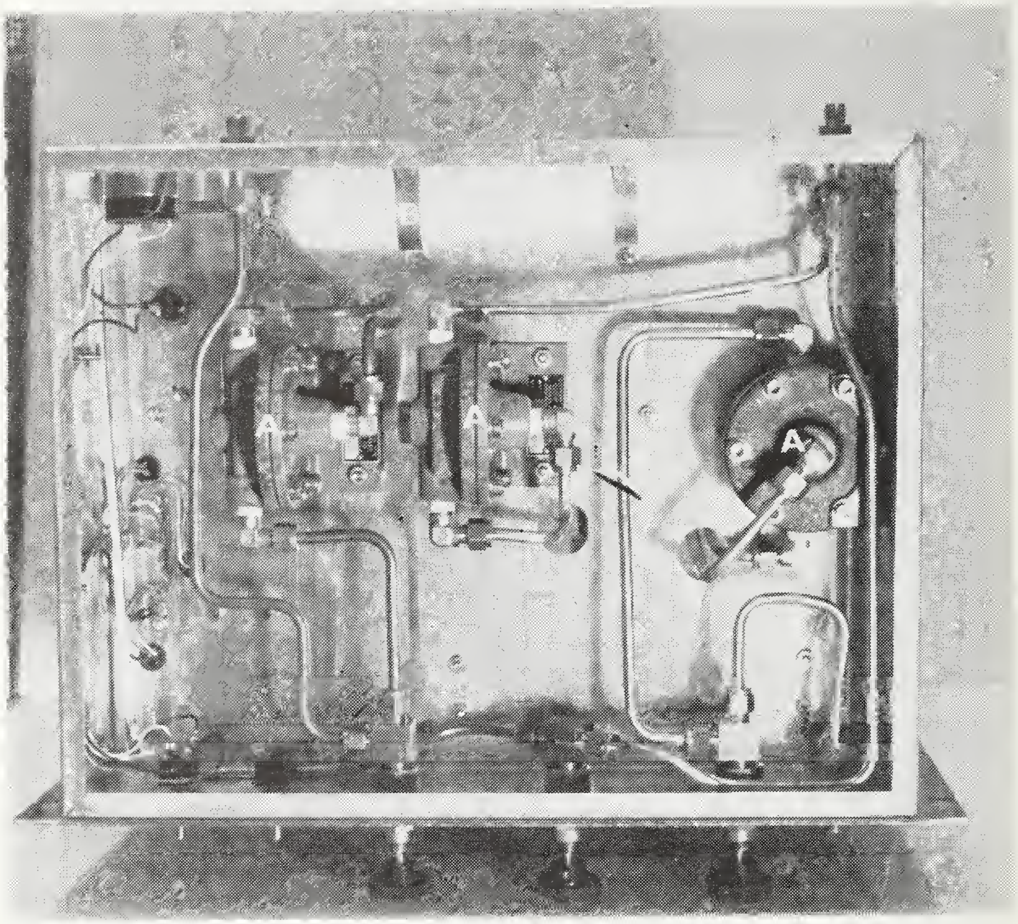

Figure 6.3 View under chassis of ammonia system
A. Differential flow controller B. Drier

sampling manifold from which a sample, or samples, may be withdrawn for analysis.

1. Gas Mixing Unit

A diagram of the gas flow system is shown in Figure 6.4. The flow of diluent air is controlled by V-1 and the flow of the bulk mixture of ammonia in air is controlled by V-2 . The flow rates are measured by means of FM-1 and FM-2, respectively. The differential flow controllers, (DFC-1) and (DFC-2), maintain a constant flow in each leg of the system after the initial setting of the flow control valves and will maintain this constant flow until these valves are readjusted. Valves 4 and 5, are shut-off valves and isolate the unit when it is not in use.

The "dryer" shown in Figure 6.4, contains both activated charcoal and silica gel and is intended as a final dryer for the diluent air.

The flow of diluent and bulk mixture combine in the mixing chamber and pass to the sampling manifold. The concentration of ammonia in the air in the manifold is calculated from the observed flow rates and from the measured concentration of ammonia in the bulk mixture. The concentration of ammonia in the bulk mixture is determined with the analytical unit.

2. Analytical Unit

A 3-way valve, (V-9), is located downstream from FM-2 in the bulk-mixture stream. In the "mixing" position the valve directs the flow to the mixing chamber. In the "analysis" position, the sample is directed to a 3-way solenoid valve

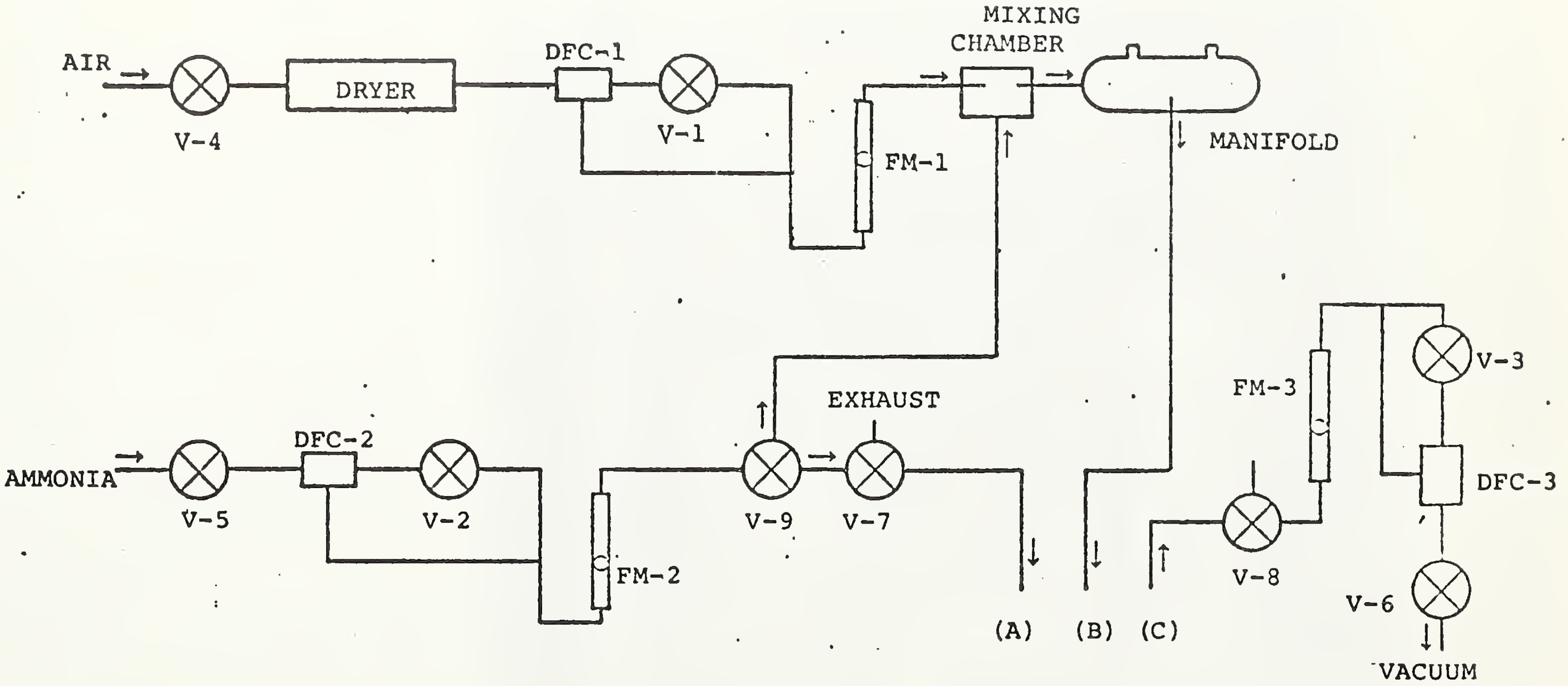

Figure 6.4 Schematic diagram of ammonia system

(V-7). In the normal position, V-7 vents the sample to atmosphere. When the solenoid is energized, the sample is directed to the glass socket joint marked (A). A midget impinger containing a measured volume of acid and an acidimetric indicator is connected to this socket. A timer is connected in parallel with the circuit which energizes V-7 as shown in the wiring diagram, Figure 6.5. When the timer switch, S-2, which also controls V-7 and V-8 is in the "on" position, the timer operates and gas flows through the impinger at the flow rate indicated by FM-2. When the titration of the acid by the ammonia in the bulk mixture is complete, as indicated by a change in color of the indicator, the solenoid is de-energized by manually turning off the timer switch so that both the flow of bulk mixture through the impinger and the timer are stopped. The length of time of the titration and the observed flow rate are used to calculate the total volume of gas which passed through the impinger. The normality and volume of the acid allow a calculation of the amount of ammonia in the measured volume of bulk mixture.

A further refinement to the system enables a sample to be drawn at a controlled flow rate from the sampling manifold. The midget impinger is connected at B and C of Figure 6.4 and the vacuum system draws the sample from the manifold as indicated. The flow is controlled with V-3 and measured with FM-3. With solenoid valve, (V-8), in the normally open position, air is drawn in through the vent at a rate controlled by V-3. When the

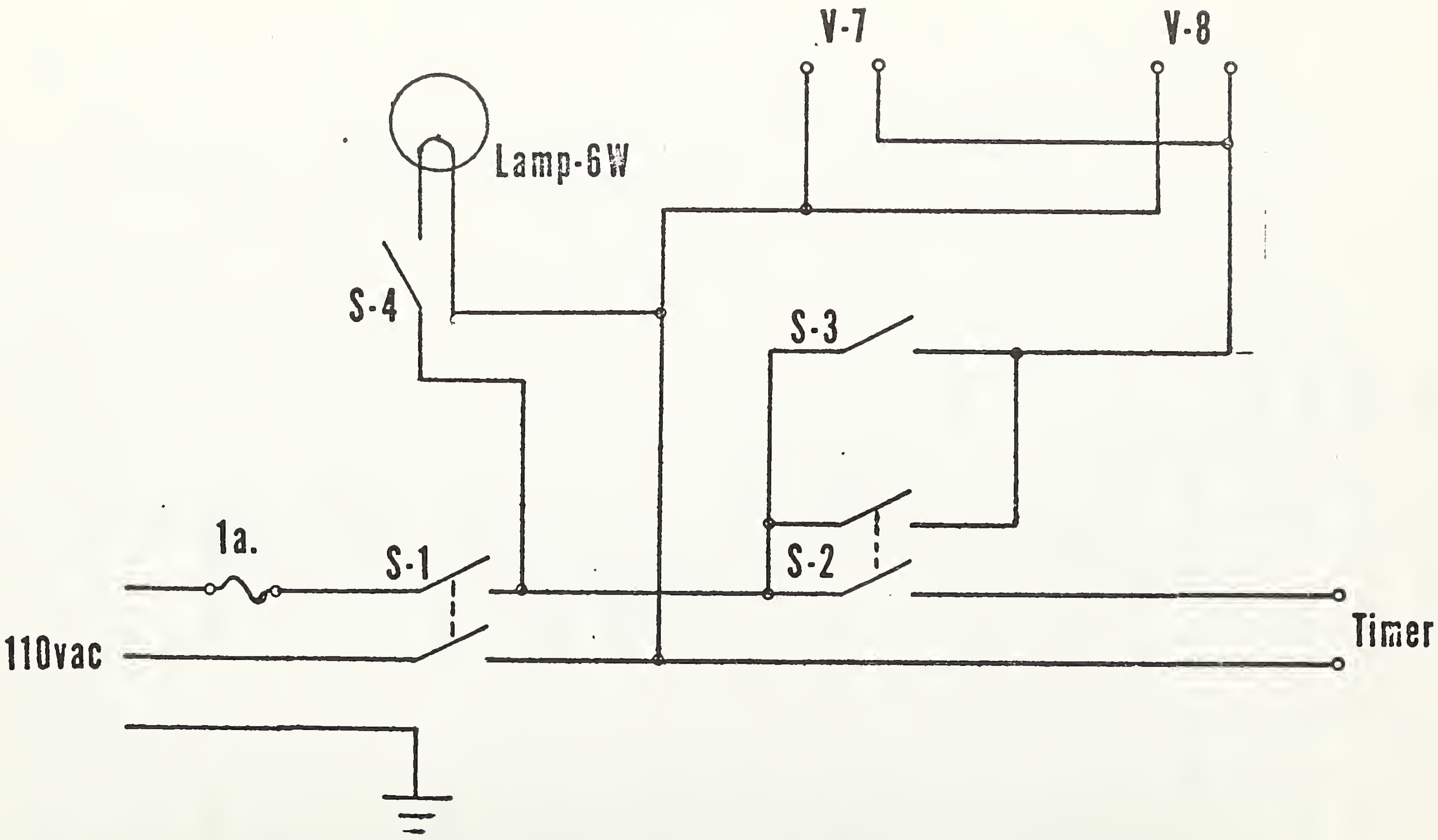

Figure 6.5 Wiring Diagram for Ammonia System.

solenoid is energized, flow is directed from the manifold at the preset rate, through the impinger and then through the control system to the vacuum line.

This portion of the system is not normally utilized but has been included to give the system more versatility should this be necessary or desirable. Titration of the diluted bulk mixture will require acid of lesser strength than is used for the bulk mixture and would require standardization of the end point at the lower concentration. No attempt should be made to dilute the acid provided with the unit for determining the concentration of dilute mixtures.

3. Gases; Gas Mixtures

A pressurized cylinder containing a bulk mixture of ammonia in nitrogen was prepared with an ammonia concentration of 1000 ppm. The cylinder was pressurized to a total pressure of 1200 psi to provide approximately 3600 liters of the 1000 ppm mixture. The source of diluent air can be either a pressurized cylinder of "breathing" air or "house" air from the bench. In either case the air is passed through a silica gel-charcoal auxilary-dryer to remove major contaminants.

4. Reagents

The solution contained in the impinger consists of 10.0 ml of 0.005 N H_2SO_4 which has been standardized and to which 2 drops of methyl purple indicator has been added.

5. Procedure

The concentration of ammonia in the bulk mixture is analyzed by determining the volume of gas required to neutralize an accurately measured volume of standardized sulfuric acid, based on the color change of the indicator. The concentration of ammonia, C_{NH_3}, in parts per million is calculated from the following equation:

$$C_{NH_3} = \frac{N \cdot v \cdot E \cdot 10^6}{F_{NH_3} \cdot t} \qquad (1)$$

where,

C_{NH_3} = ammonia concentration (ppm)

N = normality of H_2SO_4 in impinger

v = volume of H_2SO_4 (ml)

E = Molar volume (24.5 at 25°C and 760 mm pressure. If conditions differ significantly from this the value of E is given by $E = \frac{RT}{P}$ where the appropriate values of P and T are substituted.)

F_{NH_3} = ammonia flow rate (from FM-2) (cm^3/min)

t = titration time (min)

The concentration of ammonia in the dilute mixture produced when the bulk mixture of ammonia is blended with air is calculated using the following equation:

$$C_x = \frac{F_{NH_3} \cdot C_{NH_3}}{F_{NH_3} + F_{AIR}} \qquad (2)$$

where,

C_x = dilute ammonia concentration (ppm)

F_{NH_3} = bulk ammonia flow (cm^3/min)

C_{NH_3} = bulk mixture concentration (ppm)

F_{AIR} = air flow (cm^3/min)

C. Operation

1. Precautions

The maximum pressure to which the components of the system upstream of V-1 and V-2 should be subjected is 100 psi. The flow controllers (DFC-1) and (DFC-2) will not operate satisfactorily at pressures below 10 psi. Therefore, both the diluent air and the bulk mixture should be controlled at a pressure between 10 and 100 psi. A stainless steel gas cylinder regulator and a short length of flexible stainless steel tubing are provided with the unit for connecting the bulk mixture. The diluent air supply may be any source of clean and dry air at a pressure greater than 10 and less than 100 psi. The internal dryer is not intended to clean large volumes of grossly contaminated air but rather is intended to reduce residual moisture and organic vapors to a reasonably low level. Valves V-2 and V-3 are fine control valves and should never be closed more than finger tight.

2. Initial Set-Up

a. The bulk mixture, air and vacuum shut-off valves and regulator valves are closed and that the four electrical switches are in the off position.

b. Connect the air line to the air inlet at the back of the chassis.

c. Connect a vacuum line to the vacuum inlet of the chassis.

d. Connect the instrument to a 115 volt AC source.

e. Connect the bulk mixture of ammonia-in-air to the inlet on the left side of the front panel.

3. Analysis of Bulk Mixtures by Direct Sampling

The concentration of ammonia in the bulk mixture is analyzed by determining the volume of gas required to neutralize an accurately measured volume of standardized sulfuric acid. The following procedure should be used.

a. Turn the sampling valve (V-9) to "analysis".

b. Adjust the bulk mixture regulator to a pressure less than 100 psi.

c. Open the valve on the bulk mixture and adjust the ammonia flow to the desired value with (V-2) "Ammonia", on the instrument front panel. A flow rate of 365 cm^3/min (50.0 scale divisions on FM-2 using the stainless steel float) is recommended when using a bulk mixture containing approximately 1200 ppm of ammonia in air. The bulk mixture flow should be shut off at the tank when actual measurements are not being made in order to conserve the supply of this gas.

d. Turn on "AC Power" switch (S-1).

e. Turn on the "Flush" switch (S-3) for several minutes which will effectively flush air or the previous gas mixture from the sampling lines to the sample outlet on the analysis unit. The gas mixing unit is now ready for sampling directly from the bulk mixture.

f. Carefully break the neck of an ampoule containing 10 ml of the 0.005N H_2SO_4 supplied with the unit. Add the entire contents to a clean impinger tube. Add 2 drops of methyl purple indicator. Rinse the ampoule with a small amount of distilled water and add to the impinger. Add distilled water until the total volume of liquid in the impinger tube is 20 ml.

g. Make sure that the sampling line has been flushed as described in Step e, and that the "Flush" switch, (S-3) has been turned off. Attach the middle tube of the impinger to the direct sampling outlet (A) (the socket joint on the left in the sampling compartment). The side arm of the impinger tube is not connected.

h. Turn on "Lamp" switch. (The lamp should be turned on only when performing a titration to avoid heating the sample compartment.)

i. Make sure that the timer is set at 00.00 minutes by pushing the reset button on the timer.

j. Turn on the "Timer" switch (S-2). Gas will now bubble through the impinger and the timer will operate. As soon as the indicator changes from blue to the <u>final shade of green</u>, turn off S-2.

A preliminary titration should be performed, bubbling past the end-point, in order to become familiar with the color change of the indicator at the end-point. The concentration of ammonia, C_{NH_3}, in parts per million is calculated from Equation (1):

The results of the three titrations should agree to within 1 to 2 percent. The bulk mixture should be analyzed at the beginning of each day of use and whenever a new bulk mixture is introduced. Because the concentration of ammonia in the bulk mixture may change with time, the concentration as determined by titration should be used for all calculations.

4. Preparation of Dilute Air-Ammonia Mixtures

a. Turn the sampling valve (V-9) to "Mixing".

b. Determine the flow rates of air and ammonia which will yield the desired concentration using the equation in instruction 5.

c. Open the air shut off valve (V-4) and adjust the air flow with V-1, "Air", to the desired value.

d. Open the ammonia shut off valve (V-5) and adjust V-2, "Ammonia", for the desired flow of the bulk mixture. (These rotameter settings should be made before sampling in the impinger.)

e. Calculate the concentration of ammonia in the manifold, C_x, by Equation (2).

5. Shut-Down

The bulk mixture should be shut-off at the cylinder at anytime when immediate use of the system is not anticipated. This is a precaution taken to avoid loss of the bulk mixture through leakage. If the system is to be left unattended, the air, the bulk mixture, and the vacuum should be shut off by closing V-4, V-5 and V-6. If there is any possibility of external pressure from these sources entering the system and exceeding the maximum pressure of 100 psi then both the "Ammonia" and "Air" valves, (V-1) and (V-2) should be left open. The power switch, (S-1), should be in the off position whenever the system is not in use.

D. Maintenance

1. Gas Mixing Unit

The silica gel and the activated charcoal in the drying cylinder may occasionally need to be replaced depending on the purity of the house air supply and the amount of use of this unit. The drying cylinder can be removed after taking the instrument out of the cabinet by taking off the supporting straps and disconnecting the tubing at each end of the cylinder.

The cylinder may be reactivated by placing in an oven at about 110°C while passing a slow flow of clean air through the cylinder. Alternatively, the cylinder may be refilled with freshly activated silica gel and activated charcoal in the appropriate amount and order shown on the cylinder. Add sufficient glass wool so that the silica gel and charcoal are firmly packed in the cylinder. Replace the fittings and reinstall the cylinder in the chassis.

Both the gas mixing chamber and the gas sampling manifold can be easily removed by loosening the appropriate connections when repair or replacement is required.

The procedures for cleaning the rotameters and flow controllers are given in the manufacturer's instructions.

2. Analytical Unit

The lamp may be replaced after removing the four screws in the corners of the sampling compartment which hold the translucent plastic sheet in place at the back of the sampling compartment.

The electrical system is protected with a 1 ampere fuse located inside the cabinet on the top surface of the chassis. The glass connectors (A, B, and C of Figure 6.2) may be removed and replaced by loosening the Swagelok connectors and removing the retaining strap.

E. Materials of Construction

The materials of construction are brass, copper, Teflon, stainless steel, and glass. The portion of the system which is exposed to ammonia is constructed entirely of stainless steel, Teflon and glass. The diluent air system is composed primarily of copper and brass.

F. PERFORMANCE EVALUATION

1. Analysis of Bulk Mixtures

Table 6.1 shows the results of replicate analyses of samples taken directly from the bulk mixture cylinder. The sample flowed directly into the impinger without going through the sampling manifold. The precision of these analyses is very good indicating that the analytical unit is reliable. The accuracy of the analyses was confirmed by titration of several acid samples with NaOH. These analyses agree to ±1 percent of those obtained by titration with gaseous ammonia.

TABLE 6.1

Direct Analysis of Bulk Mixture

Sample	Titration Time	ppm NH_3
1	2.74	1232
2	2.73	1236
3	2.73	1236
4	2.72	1241
5	2.72	1241
6	2.73	1236
7	2.73	1236
8	2.73	1236
9	2.72	1241
10	2.73	1236
average	2.728	1237.1
standard deviation	.006	3.0
rel. std. dev.	0.23%	0.24%

conditions of analysis:

F_{NH_3}------------------375 cm^3/min
N--------------------.005165
v--------------------10.0 ml
E--------------------24.5

2. Stability of Bulk Mixtures

The bulk mixtures of ammonia in nitrogen were re-analyzed periodically over a period of 5 months with less than 1 percent change in concentration indicating that high concentration ammonia mixtures have good long-term stability and can be stored in pressurized cylinders. Even if the mixtures should deteriorate, this would pose no problem for re-analysis of the bulk mixtures can be done quite easily with the analytical unit of the instrument.

3. Analysis of Ammonia-Air Dilutions

Various mixtures of ammonia in air were prepared by dilution and analyzed. Table 6.2 shows a comparison of the concentration calculated from air and ammonia flows with that obtained by analysis. The average difference is 1 percent with no bias in either direction.

4. Effect of Sampling Rate

Figure 6.6 shows the effect of the rate of withdrawal of sample from the sampling manifold on the analysis. The apparent decrease in ammonia concentration at higher flow rates is probably due to incomplete absorption of the ammonis in the impinger solution. For this reason, sampling should be done at a rate less than 700 cm^3/min.

TABLE 6.2

Analysis of Ammonia-Air Dilutions

Concentration (ppm)			
Calculated	Analyzed	Difference	Diff. in Percent
35.6	35.2	-0.4	1.1
36.1	36.3	+0.2	0.6
52.1	52.5	+0.4	0.8
52.1	51.8	-0.3	0.6
52.1	53.0	+0.9	1.7
93.9	95.7	+1.8	1.9
100.1	99.2	-0.9	0.9
100.6	104.0	+3.4	3.3
243.3	242.0	-1.3	0.5

Ammonia Bulk Mixture = 1272 ppm

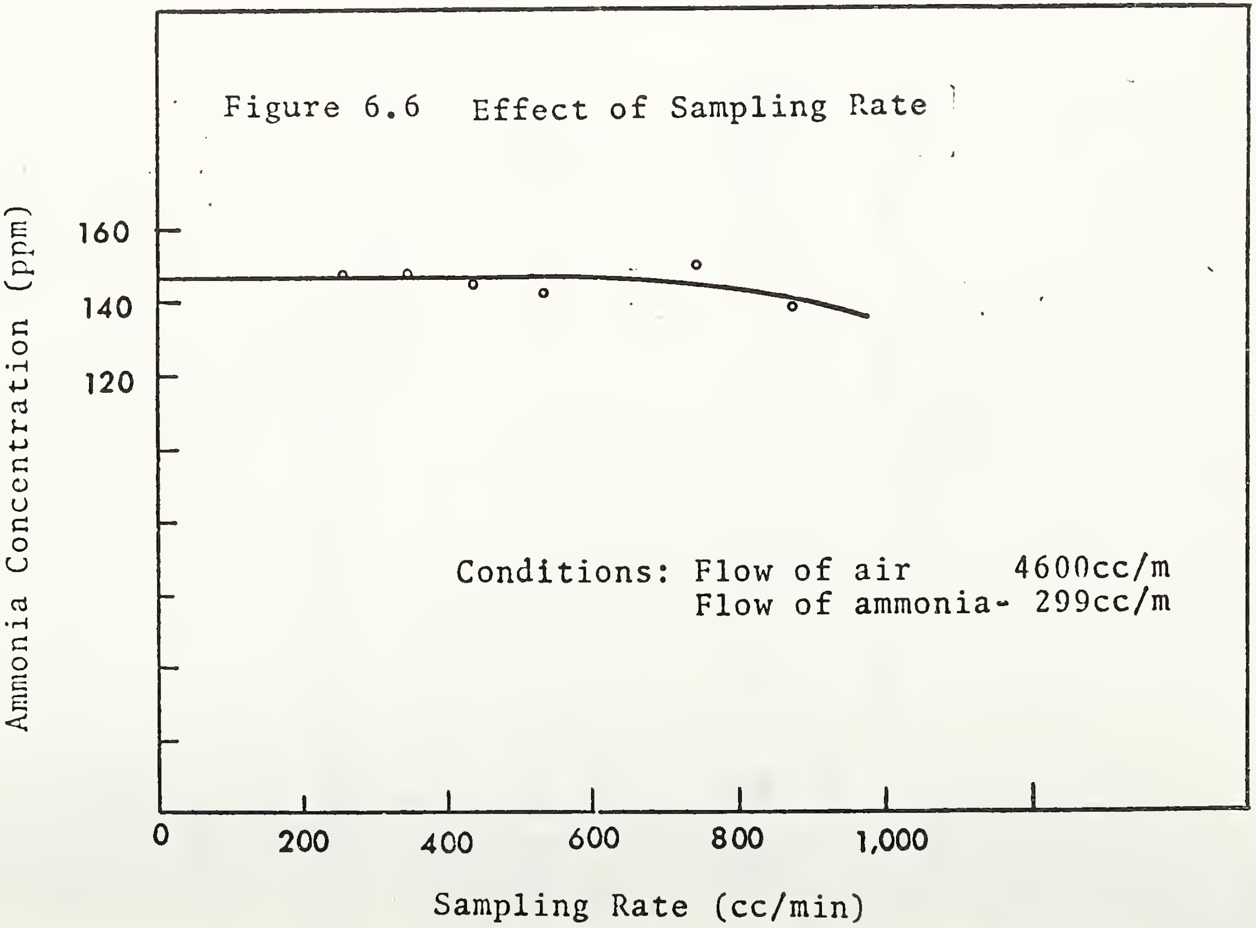

Figure 6.6 Effect of Sampling Rate

G. CONCLUSIONS

The system described in this report is capable of producing test atmospheres of varying concentrationsof ammonia in air by blending a bulk mixture of ammonia in nitrogen from a pressurized cylinder with a stream of diluent air. Analysis can be easily performed by titrating a standard acid sample with the ammonia in the gas stream.

It should be possible to adapt this system to the generation and analysis of other gas mixtures as long as the bulk mixture possesses adequate tank stability and a titration reaction can be performed in the analysis.

7. CHLORINE SYSTEM

A. Introduction

This system produces mixtures of chlorine in air over a wide concentration range. The system combines two units; a gas blending unit and an analytical unit. The gas blending unit produces low concentrations of chlorine by diluting a relatively high concentration of chlorine in nitrogen (*i.e.* the bulk mixture) with a stream of clean, chlorine-free air, (*i.e.* the diluent). The analytical unit consists of a system which directs the bulk mixture through an impinger where the chlorine is collected after which it is determined colorimetrically. Analysis of the bulk mixture prior to use serves to confirm that the mixture has not deteriorated between analysis or serves to assess the extent of deterioration.

B. Principle of Operation

A photograph of the system is shown in Figure 7.1. The location of principal parts is shown in Figure 7.2. The gas cylinder containing the bulk mixture is connected to the bulkhead connector on the front panel marked "chlorine inlet." The diluent air is connected at the rear of the chassis at the connector marked "air in." The bulk mixture and the diluent air are mixed in known proportions and are directed to the sampling manifold from which a sample, or samples, may be withdrawn.

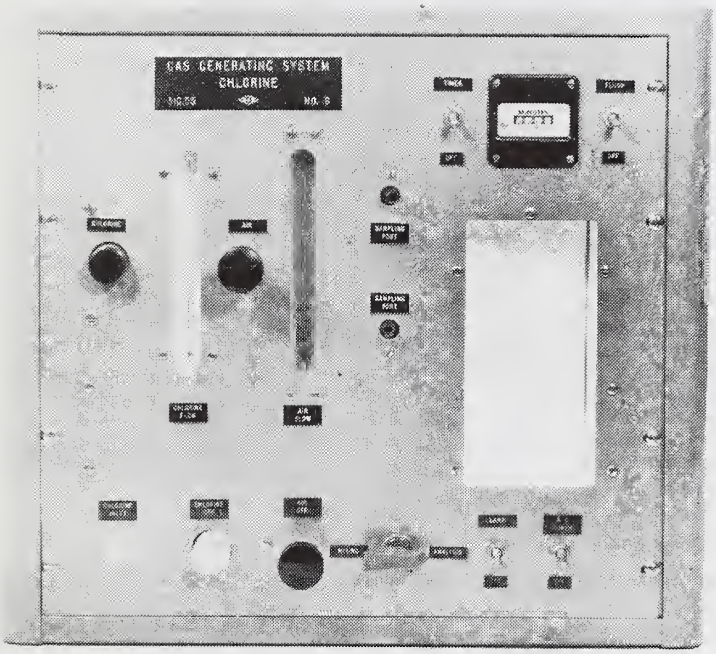

Figure 7.1 Photograph of chlorine system

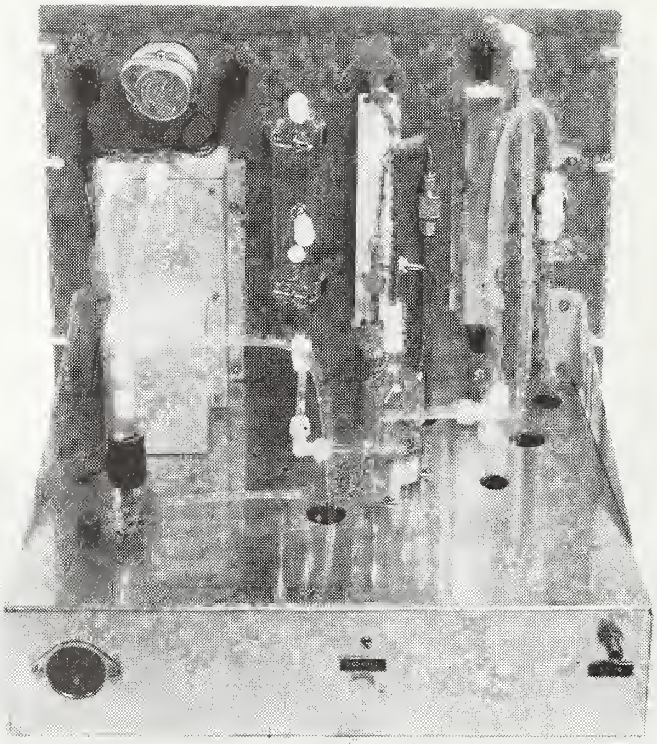

Figure 7.2 Interior view of chlorine system

1. Gas Blending Unit

The gas flow system is shown in Figure 7.3. The flow of diluent air is controlled by adjustment of V-1 and the flow of the bulk mixture of chlorine in air is controlled by V-2. The flow rates are measured at FM-1 and FM-2, respectively. The differential flow regulator (DFC-1) maintains a constant flow in the diluent side of the system depending on the setting of the flow control valve (V-1). Valves (V-4) and (V-5) are shut-off valves and isolate the unit when it is not in use.

The "dryer" shown in Figure 7.3, contains both activated charcoal and silica gel and is intended as a final dryer for the diluent air.

The diluent and bulk mixtures combine in the mixing chamber and pass to the sampling manifold. The concentration of chlorine in the air in the manifold is calculated from the observed flow rates and from the measured concentration of chlorine in the bulk mixture as determined with the analytical unit.

2. Analytical Unit

A three-way valve (V-3) is located downstream from FM-2 in the bulk mixture stream. In the "mixing" position the valve directs the flow to the mixing chamber. In the "analysis" position, the sample is directed to a three-way solenoid valve (V-6). In the normal position V-6 vents the sample to the

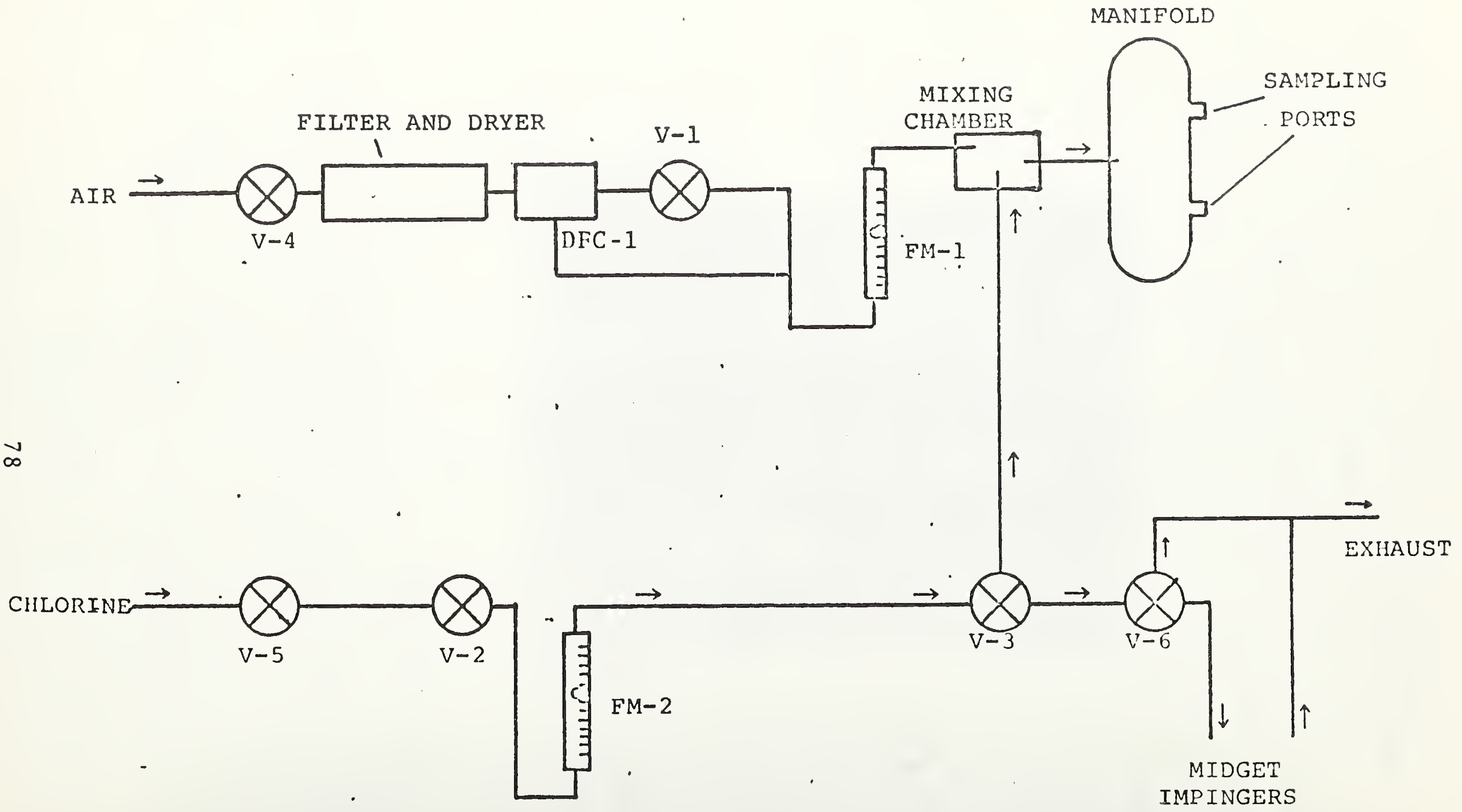

Figure 7.3 Schematic Diagram of Chlorine System.

exhaust port. When the solenoid is energized, the sample is directed to the glass socket joint. A midget impinger containing an absorbing solution is connected to this socket. A timer is connected in parallel with the circuit which energizes V-6 as shown in the wiring diagram, Figure 7.4. When S-2, which controls V-6, is in the "on" position, gas flows through the impinger at the flow rate indicated by FM-2 and the timer operates. The solenoid is de-energized by opening S-2 so that both the flow of bulk mixture through the impinger and the timer are stopped. The time measurement and the observed flow rate allow a calculation of the total volume of gas which passed through the impinger.

3. Gases, Gas Mixtures

A pressurized cylinder containing a bulk mixture of chlorine (99+ percent) in nitrogen was prepared with a chlorine concentration of 50 ppm. The cylinder was pressurized to a total pressure of 1200 psi which means that approximately 3600 liters of the 50 ppm mixture are available. The source of diluent air can be either a pressurized cylinder of "breathing" air or "house" air from the bench. In either case, the air is passed through a silica gel-charcoal dryer to remove major contaminants. An external pre-drier may be required if "house" air is used.

4. Procedure

The concentration of chlorine in the bulk mixture may be determined by passing a known volume of the gas through a solution contained in the impinger producing a color change

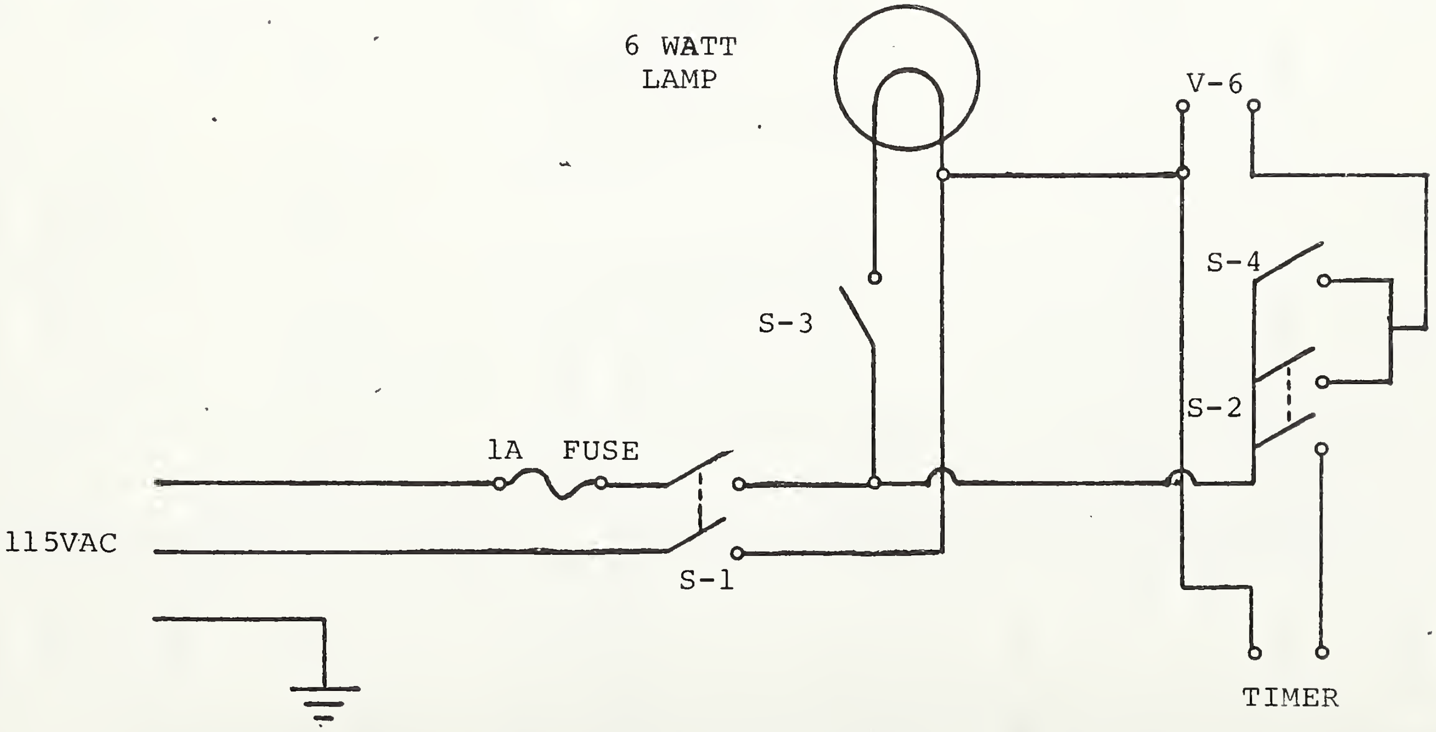

Figure 7.4 Wiring Diagram - Chlorine System.

which is determined spectrophotometrically and is related to the chlorine content of the sample. An alternate method of analysis consists of titrating a standardized thiosulfate solution, contained in neutral-buffered potassium iodide, with the gaseous chlorine mixture to a starch-iodine end point.

In the spectrophotometric method, the chlorine concentration is determined by comparison to a calibration curve, whereas in the thiosulfate titration, the chlorine concentration is determined by use of the following equation:

$$C_{Cl_2} = \frac{1/2\ N \cdot v \cdot E \cdot 10^6}{F_{Cl_2} \cdot \Delta t} \qquad (1)$$

where,

C_{Cl_2} = chlorine concentration (ppm).

N = normality of thiosulfate solution.

v = volume of thiosulfate (ml).

E = molar volume (24.5ℓ at 25°C and 760 mm pressure. If conditions differ significantly from this, the value of E is given by $E = RT/P$, where the appropriate values of P and T are substituted.

F_{Cl_2} = chlorine flow rate (from FM-2) (cm^3/min).

Δt = titration time - blank time (min).

The concentration of chlorine in the dilute mixtures produced when the bulk mixture of chlorine is blended with air is calculated using the following equation:

$$C_x = \frac{F_{Cl_2} \cdot C_{C.2}}{F_{Cl_2}} \qquad (2)$$

C_x = dilute chlorine concentration (ppm).

F_{Cl_2} = bulk chlorine flow (cm^3/min).

C_{Cl_2} = bulk mixture concentration (ppm).

F_{AIR} = diluent air flow (cm^3/min).

C. Operation

1. Precautions

The maximum pressure to which the components of the system upstream of V-1 should be subjected is 100 psi. The flow controller (DFC-1) will not operate satisfactorily at pressures below 10 psi. Therefore, the diluent air should be controlled at a pressure between 10 and 100 psi. A gas cylinder regulator with a monel diaphragm and a short length of flexible Teflon tubing are provided with the unit for connecting the bulk mixture. The diluent air supply may be any source of clean, dry air at a pressure greater than 10 and less than 100 psi. The internal dryer is not intended to clean large volumes of grossly contaminated air but rather is intended to reduce residual moisture and organic vapors to a reasonably low level. Valve V-2 is a fine control valve and should never be closed more than finger tight.

2. Initial Set-Up

a. Be sure that the bulk mixture and air shut-off valves and regulator valves are closed and that the four electrical switches are in the off position.

b. Connect the air line to the air inlet at the back of the chassis.

c. Connect an exhaust line to the exhaust port at the back of the chassis.

d. Connect the instrument to a 115 volt AC source.

e. Connect the bulk mixture of chlorine-in-nitrogen to the inlet on the left side of the front panel.

3. Analysis of Bulk Chlorine Mixtures

a. Turn the sampling valve (V-3) to the "analysis" position.

b. Adjust the bulk mixture regulator to a pressure less than 10 psi.

c. Open valve V-5 and the chlorine flow valve(V-2).

d. Coarsely adjust the flow of chlorine to the desired value using the chlorine flow valve (V-2).

e. Fine adjustment of the chlorine flow is made using the pressure control on the chlorine bulk mixture regulator. (A flow rate of 100 cm^3/min (11.1 scale divisions on the chlorine rotameter using the stainless steel float, is recommended). The bulk mixture flow should be shut off at the tank when actual measurements are not being made in order to conserve the supply of this gas.

f. Turn on the AC power switch (S-1).

g. Turn on the flushing switch (S-4) for at least 15 minutes which will effectively flush air or the previous gas mixture from the system. The gas mixing unit is now ready for sampling directly from the bulk mixture.

4. Analysis of Bulk Mixtures

This method is essentially the titration of a standard thiosulfate solution with a chlorine in nitrogen gas mixture using starch as the indicator.

Steps a. thru h. establish a blank needed for the chlorine analysis which is given in steps i. thru r.

a. Place 5.0 ml of the neutral buffered KI solution in the impinger.

b. Add 2 ml starch solution.

c. Dilute to 20 ml with distilled water.

d. Make sure the sampling line has been flushed as described in Step g, Section 3, and that the flush switch (S-4) has been turned off. Attach the impinger to the sample outlet.

e. Make sure that the timer is set at 00.00 minutes by pushing the reset button on the timer.

f. Turn on the timer switch, (S-2). Gas will now bubble through the impinger and the timer will operate.

g. As soon as the first indication of a faint purple color appears in the solution, turn the timer off.

h. Perform the titration three times. An agreement of ±3 percent in the time required for three titrations is an adequate blank. The average of these three times is later subtracted from the time required for titration of a sample in the procedure described below in steps i. through r.

i. Place 5.0 ml of the neutral buffered KI solution in an impinger.

j. Add 2 ml starch solution.

k. Add contents of the standard thiosulfate ampoule (1.035×10^{-4} N, volume = 10.0 ml).

l. Rinse with distilled water.

m. Dilute to 20 ml with distilled water.

n. Make sure the sampling line has been flushed as described in Step g, Section 3, and that (S-4) has been turned off. Attach the impinger to the sampling outlet.

o. Make sure that the timer is set at 00.00 minutes by pushing the reset button on the timer.

p. Turn on the timer switch, (S-2). Gas will now bubble through the impinger and the timer will operate.

q. As soon as the first indication of a faint purple color appears in the solution, turn the timer off.

r. Perform the titration three times. The times of the three titrations should agree to within 3 percent.

The titration blank obtained earlier is subtracted from this value and the concentration of chlorine in nitrogen in the bulk mixture is determined by the use of Equation (1). The bulk mixture should be analyzed at the beginning of each day of use and whenever a new bulk mixture is introduced. Because the concentration of chlorine in the bulk mixture may change with time, the concentration as determined by titration should be used for all calculations.

5. Preparation of Dilute Air-Chlorine Mixtures

a. Turn the sampling valve, (V-3), to the mixing position.

b. Determine the flow rates of air and chlorine which will yield the desired concentration.

c. Open the air-off valve (V-5) and adjust the chlorine flow valve (V-2) and the control valve on the chlorine bulk mixture regulator (V-7) for the desired flow of the bulk mixtures.

6. Shut-Down

The bulk mixture should be shut off at the cylinder at all times when immediate use of the system is not anticipated. This is a precaution taken to avoid loss of the bulk mixture through leakage. If the system is to be left unattended and it is not feasible to disconnect the diluent air and the bulk mixture, then the system should be isolated by closing the chlorine-off valve, the air-off valve and the control valve on the chlorine stock tank regulator. If there is any possibility of external pressure from these sources entering the system and exceeding the maximum pressure of 100 psi, then both the air flow valve and the chlorine flow valve should be left open.

The AC power switch, (S-1), should be in the off position whenever the system is not in use.

D. Maintenance

1. Gas Mixing Unit

The silica gel and activated charcoal in the drying cylinder may occasionally need to be replaced depending on the purity of the house air supply and the amount of use of this unit. After removing the system from the cabinet the drying cylinder can be dissembled by taking off the supporting straps and disconnecting the fittings on each end of the cylinder.

The cylinder may be reactivated by placing it in an oven at 110°C while passing a slow flow of clean air through it. Alternatively, the cylinder may be refilled with freshly activated silica gel and activated charcoal in the appropriate amount and order shown on the cylinder. When refilling the cylinder, be certain that sufficient glass wool is used so that the silica gel and charcoal are firmly packed in the cylinder.

Both the gas mixing chamber and the gas sampling manifold can be removed easily by loosening the appropriate connections in case repair or replacement is required.

2. Chlorine Analysis Unit

The lamp may be replaced after removing the four screws in the corners of the sampling compartment which hold the translucent plastic sheet in place at the back of the sampling compartment.

The electrical system is protected with a 1 ampere fuse located inside the cabinet on the top surface of the chassis. The glass connectors may be removed and replaced by loosening the connectors and removing the retaining strap.

E. Materials of Construction

The materials of construction are brass, copper, Teflon, stainless steel, and glass. The portion of the system which is exposed to chlorine is constructed entirely of stainless steel, Teflon and glass. The diluent air system is composed primarily of copper and brass.

F. PERFORMANCE EVALUATION

1. Conditioning of Gas Cylinders

Mixtures of chlorine in nitrogen placed in pressurized steel cylinders will show a decrease in chlorine concentration with time. This decrease can be slowed down considerably by conditioning the cylinder by prior exposure to a chlorine mixture of slightly greater concentration than the final mixture. If the cylinder is conditioned with a chlorine mixture of greater concentration than the final mixture, the concentration will increase with time, whereas, if the cylinder is conditioned with a mixture of lower concentration, the concentration will decrease with time. This behavior indicates that an adsorption-desorption process of chlorine onto the cylinder walls is taking place.

2. Tank Stability

Once the cylinder is conditioned properly and allowed to reach equilibrium, the change in concentration with time is fairly slow. But, because a change is continually occuring, analysis of the bulk mixture is advised before each day's operation.

3. Analysis of Bulk Mixtures

Several different analytical methods were investigated for the analysis of chlorine in air. These were as follows:

(1) o-tolidine

(2) methyl orange

(3) neutral buffered KI spectrophotometric

(4) KI-starch indicator

In methods 1, 2 and 3 an absorbing solution is placed in an impinger and the chlorine-air mixture is bubbled through this solution for a pre-determined time period. A portion of this solution is then placed in a cuvette in a spectrophotometer and the absorbance read at the appropriate wave length. The chlorine concentration is then determined by the use of a calibration curve made using known chlorine mixtures. The sensitivities of these three methods are compared in Figure 7.5.

Figure 7.5 shows the o-tolidine method to be the most sensitive. A problem arises, however, in the use of this method. Complete absorption of the chlorine in the impinger solution does not occur which produces consistently low results. This can be corrected by using two impingers connected in series. Typical results are: 80-90 percent absorption in the first impinger.

The methyl orange method requires some care in the preparation of the impinger solution. Good reproducibility in the analyses is not obtained unless the methyl orange concentration is exactly the same each time a new solution is made.

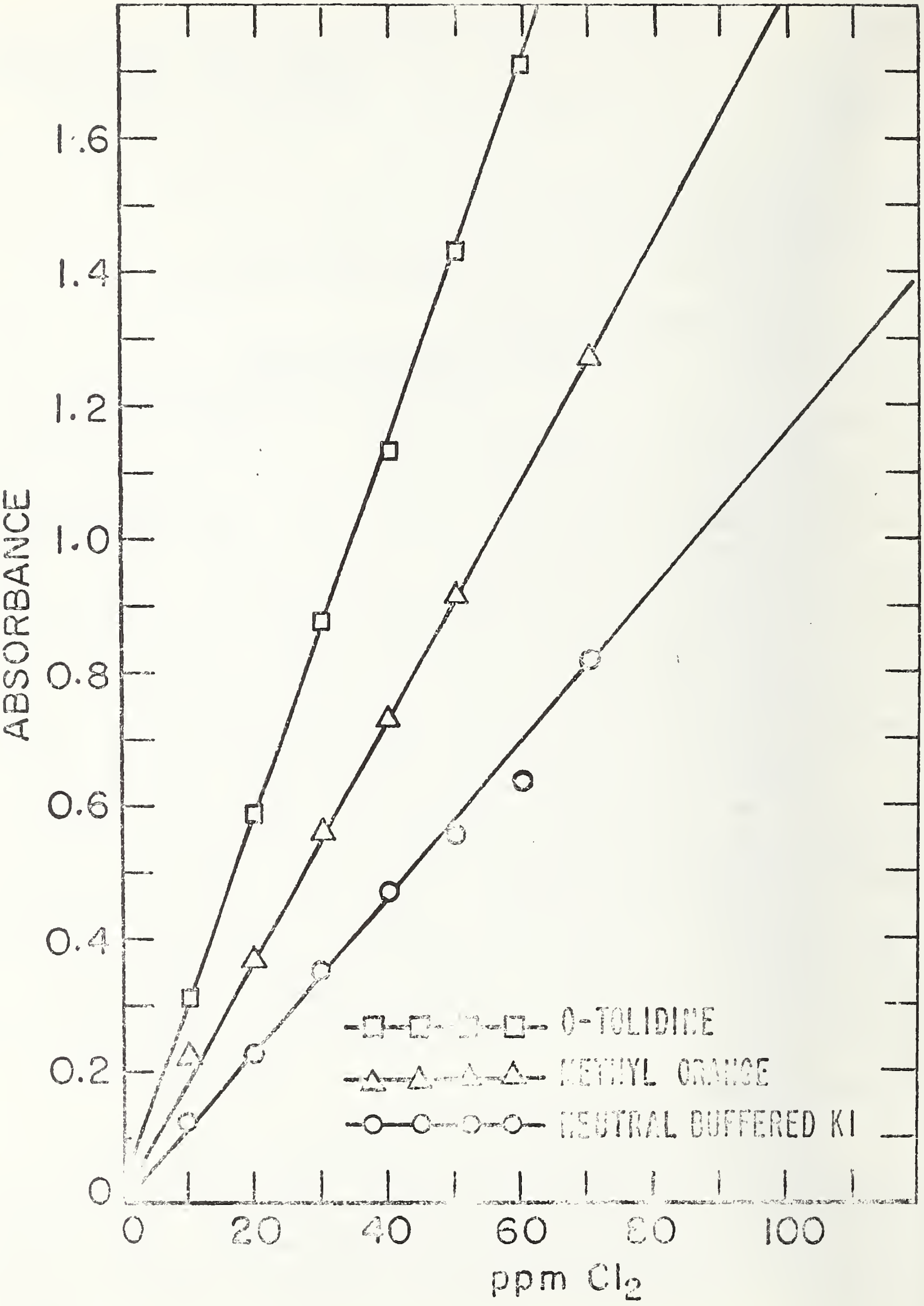

Figure 7.5 Comparison of Analytical Methods for Chlorine Analysis

The preparation of the KI solutions are less critical and complete absorption occurs in the first impinger. Since the bulk mixture concentration of chlorine should be 50 ppm ±50 percent, the neutral buffered KI method is recommended for analysis of dilute mixtures since it possesses adequate sensitivity and is easy to perform.

The KI-starch indicator method provides a way of titrating the chlorine gaseous bulk mixture to a color change at the end point. This method is also recommended and is described earlier in this report. The KI-starch indicator is not recommended for the analysis of chlorine mixtures below 10 ppm chlorine.

G. CONCLUSIONS

The system described in this report is capable of producing well-defined test atmospheres of varying concentration of chlorine in air by blending a bulk mixture of chlorine in nitrogen from a pressurized cylinder with a stream of diluent air. Analysis can be easily performed by titrating a standardized thiosulfate solution to a starch end point with the chlorine in the gas stream, or by measuring the color produced spectrophotometrically.

8. GAS HUMIDIFICATION SYSTEM

A. Principle of Operation

The gas humidification system or "saturator" is designed to deliver a stream of air with water content ranging from 100 to 15 percent relative humidity (RH). The saturator was developed to supply the ozone generator with air of known humidity or to supply the gas mixing system with humid air, which is added to the binary gas mixture produced with that unit. It may be used with any other system where air of known humidity is required.

Varying humidities are produced in the stream of delivered air by saturation at elevated pressure followed by expansion to atmospheric pressure. The relationship between the saturation pressure, P_s, the delivery pressure, P_d, and the RH is:

$$RH = \frac{P_d}{P_s} \times 100.$$

This equation accurately describes the relative humidity of the delivered air providing that the temperature of the saturator and the temperature of the delivered air are the same and that the pressures are expressed in the same units. In practice, this will be the case since both saturator, and the unit to which the humid air is delivered will be at the same temperature.

B. Description of System

The saturator is shown schematically in Figure 8.1 while Figure 8.2 and 8.3 are photographs of the front and interior of the unit. Clean air enters the system at A, and passes through the regulator to V-4. When V-4 is opened, the pressure in the saturators is determined by the setting of the regulator and is indicated by the gauge. Air saturated at the indicated pressure is expanded to atmospheric pressure across V-5 and the flow is indicated by the flow meter FM-1. Connection to the ozone generating system, or other system, is made from "B" on humidifier to the appropriate position on the other system.

C. Operation

1. Close valves marked "Air On" (V-4) and "Air Control" (V-5).

2. Unscrew handle of regulator to full counter clockwise position. Handle will fall off if unscrewed too far. If this happens merely screw back in a couple of turns.

3. Connect 1/4 in copper tubing between supply of clean dry compressed air at a pressure greater than 10 psi and less than 150 psi at connection marked "Air In".

4. Connect 1/4 in copper tubing between "Air Out" on humidifier and the system to which the humid air is to be added.

5. Turn on the air supply.

6. Open fully valve marked "Air On" (V-4) on the humidifier.

Caution: Never open (V-4) valve unless the pressure gauge reading is "zero".

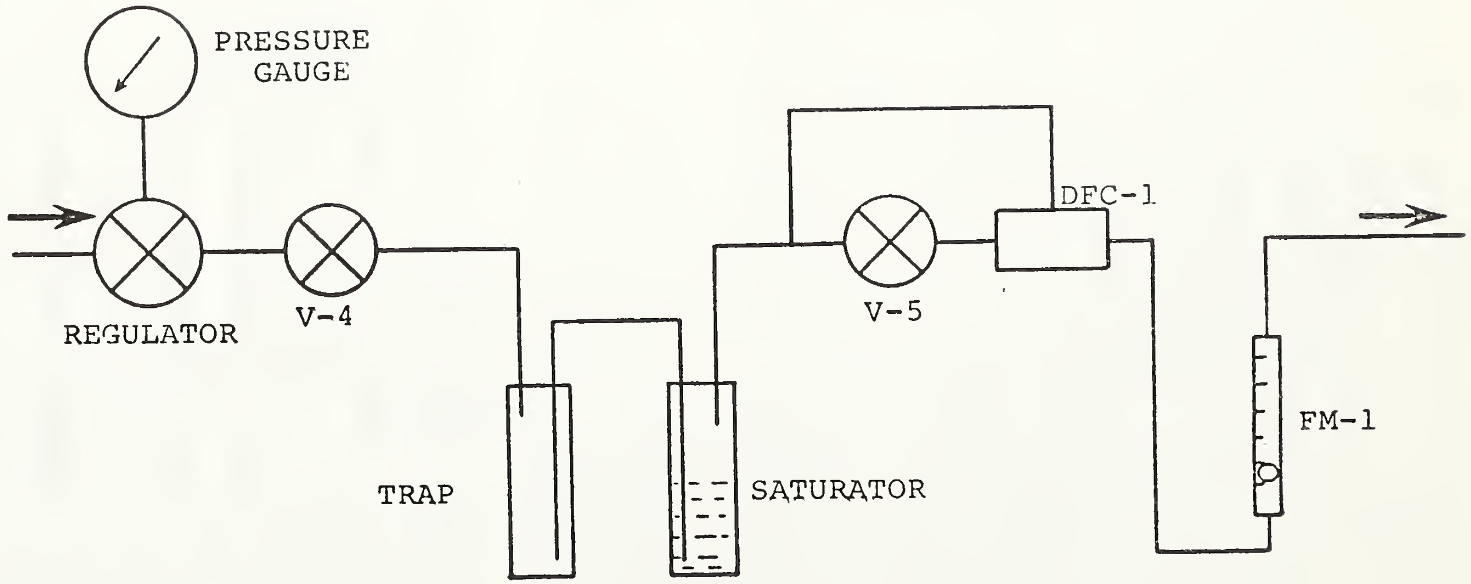

Figure 8.1 Schematic Diagram of Humidifier.

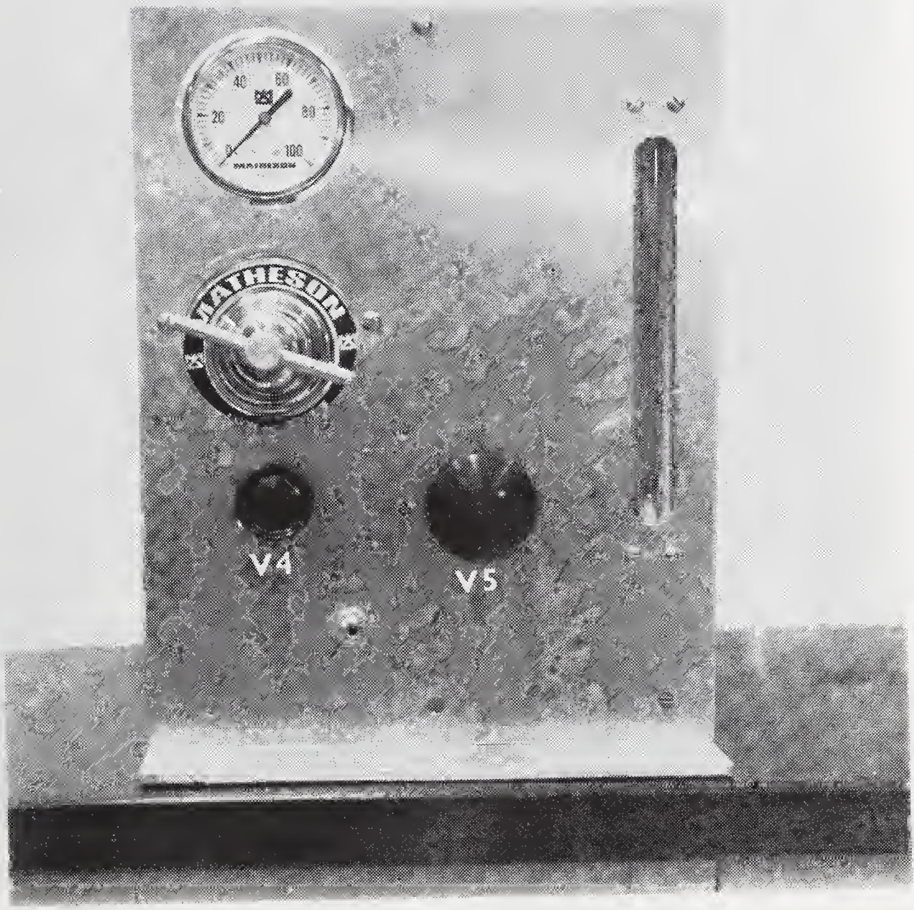

Figure 8.2 Front view of humidifier

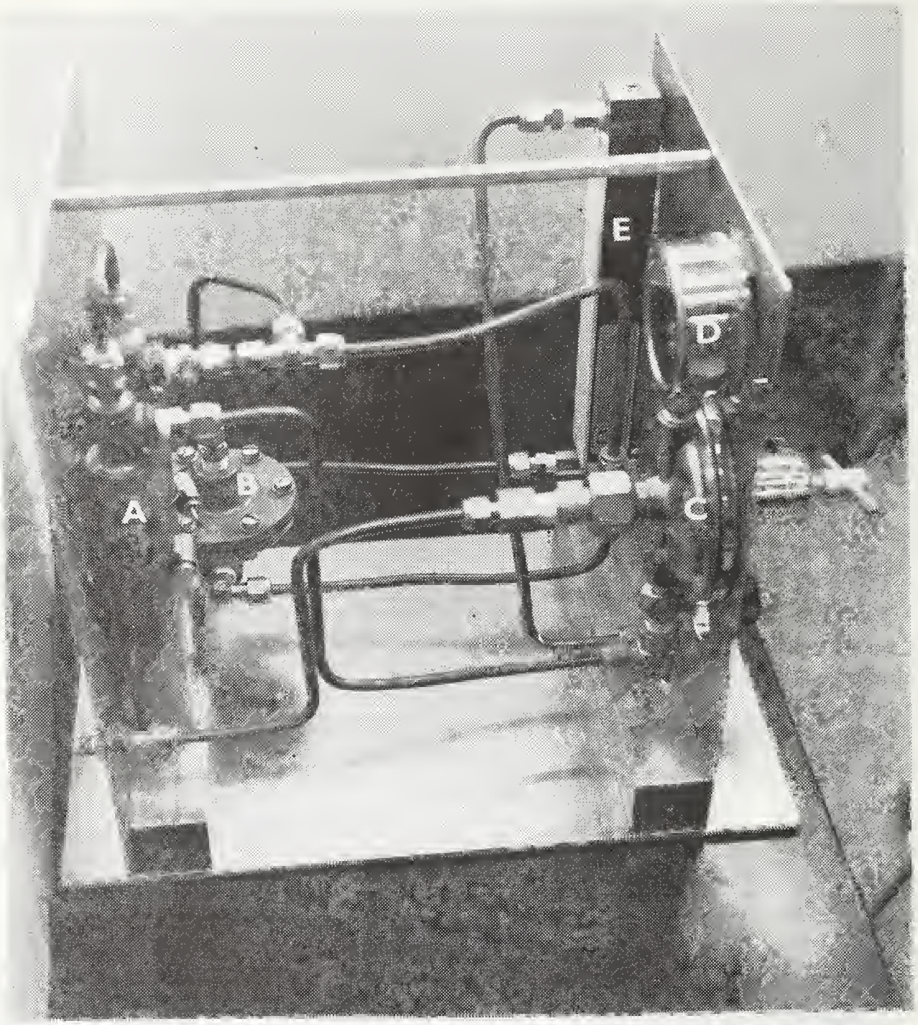

Figure 8.3 Side view of humidifier

A. Saturator B. Differential flow controller
C. Regulator D. Pressure gage E. Flowmeter

7. Turn handle of regulator until desired saturation pressure is attained. Relative humidity and pressure relationship are shown below:

Saturation Pressure, psig	Percent Relative Humidity
5	75
15	50
30	33
45	25

8. Slowly open "Air Control" (V-5) to produce desired flow rate.

D. Maintenance

Both the trap and the saturator are filled with fine gravel and the saturator should contain about 10 to 20 ml of liquid water at the beginning of any period of use. A liter of air saturated at one atmosphere contains about 25 mg of water and an initial filling of 10 ml in the saturators should be sufficient to humidify about 400 liters of air to a relative humidity of 100 percent. Larger volumes can be humidified at lower relative humidities. In any case, water should be added to the saturators periodically during use. The connection between the tops of the two saturators is removed and water is added until the level in each saturator is about 1/3 the height of the saturator body. Water can be added conveniently with a large syringe to which is attached a length of 1/16 in flexible tubing. The water level can be adjusted after addition of excess water by positioning the flexible tube in the center tube of each saturator so that the end of the flexible tube is 1/3 of the height of the saturator from the bottom of the saturator. The syringe is held in this position and water is withdrawn to the bottom of the tube.

9. PARTS LIST

Whenever possible, commercially available parts have been used in the systems described in this report. These parts were chosen primarily for availability and function. Any similar parts from manufacturers other than those shown which have the proper operating characteristics can be substituted for those listed in Table 9.2. This table lists the part number, a description, the manufacturer, and either a catalog number or manufacturers designation. Table 9.1 identifies the individual components on the schematic diagrams.

Replacement of parts which are not commercially available and which were made especially for these systems may be obtained from the National Bureau of Standards at the cost of fabrication. Alternatively, they may be fabricated as needed by the user. None of these parts are dimensionally critical and an understanding of their function and approximate dimensions should be sufficient to allow their duplication. Sketches and dimensions are available on request from the National Bureau of Standards.

Table 9.1 Key to Parts Shown on Schematic Diagrams

Figure Number	Component	Part Number-Table 9.2
2.1	V-1,2,3,4,	100-1 or 100-2
Filter	Filter	400-1
	Flowmeter	200-1
3.4	V-1	100-10
	V-2	100-3
	V-3,5	100-9
	V-4	100-11
	V-6,7,8,	100-12
	V-9	100-7
	DFC-1	300-1
	DFC-2,3	300-2
	FM-1	200-3
	FM-2,3	200-4
	Pump	500-1
	Filter	400-1
4.2	V-1,3	100-2
	V-2	100-1
	DFC-1	300-1
	FM-1	200-3
5.3	V-1,3,4	100-2
	V-2,5	100-1
	DFC-1	300-5
	Flowmeter	200-2
6.4	V-1	100-3
	V-2,3	100-4
	V-4,5,6	100-5
	V-7,8	100-6
	V-9	100-7
	DFC-1	300-1
	DFC-2	300-2
	DFC-3	300-3
	FM-1	200-3
	FM-2,3	200-4
6.5	S-1,2	500-2
	S-3,4	500-3
	Timer	500-4
	V-7,8	100-6

Table 9.1 continued.

Figure Number	Component	Part Number-Table 9.2
7.3	V-1	100-1
	V-2	100-14
	V-3	100-16
	V-4	100-2
	V-5	100-15
	V-6	100-6
	DFC-1	300-2
	FM-1	200-3
	FM-2	200-6
	Filter	400-1
7.4	S-1,2	500-2
	S-3,4	500-3
	Timer	500-4
	V-6	100-6
8.1	V-4	100-1
	V-5	100-8
	DFC-1	300-4
	FM-1	200-5
	Regulator	500-5

Table 9.2 List of Commercially Available Parts.

Part Number	Description	Manufacturer*	Designation or Cat. No.
100-1	Valve	Whitey	1RS4
100-2	Valve	Whitey	1VS4
100-3	Valve	Whitey	31RS4
100-4	Valve-micro metering	Whitey	22RS4
100-5	Valve	Whitey	3NBS4
100-6	Valve-solenoid	Skinner	B3DA1150
100-7	Valve-3 way	Whitey	42X54
100-8	Valve	Whitey	4RS4
100-9	Valve	Whitey	3NBS4A316
100-10	Valve	Whitey	3VS4
100-11	Valve	Whitey	22RS4316
100-12	Valve-3 way	Whitey	31RS4316
100-13	Valve-3 way	Whitey	42XS4316
100-14	Valve-Nylon	Nupro	Z-4V
100-15	Valve-Teflon	Nupro	T-4VD
100-16	Valve-monel	Hoke	7165G4M
200-1	Flowmeter-Flotronic	Matheson	8112-0113
200-2	Flowmeter	Hastings-Raydist	A11-5KX
200-3	Rotameter	Brooks	R-2-15-C
200-4	Rotameter	Brooks	R-2-15-D
200-5	Rotameter	Brooks	R-2-15-B
200-6	Rotameter	Matheson	Tube no. 300
300-1	Flow controller	Moore	63BD
300-2	Flow controller	Moore	63SDL
300-3	Flow controller	Moore	63BUL
300-4	Flow controller	Moore	63BU
300-5	Flow controller	Moore	63BDL
400-1	Line filter	Nupro	4F-60
500-1	Diaphragm pump	Neptune	Model 2
500-2	Toggle switch-DPST		
500-3	Toggle switch-SPST		
500-4	Timer	Precision Timer	SR-240-3
500-5	Regulator	Matheson	40H

*Mention of manufacturer does not constitute a recommendation or endorsement by the NBS nor does it imply that the material or equipment is necessarily the best available for the purpose.

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16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

This report summarizes a project concerned with the design, testing and calibration of systems for producing known low concentrations of a number of substances in air at concentrations in the vicinity of the TLV (Threshold Limit Value). The substances include carbon dioxide, carbon monoxide, ozone, sulfur dioxide, hydrogen sulfide, nitrogen dioxide, benzene, carbon tetrachloride, trichloroethylene, tetrachloroethylene, ammonia and chlorine. The systems are of four basic types: direct delivery from cylinders of known concentration, dynamic blending of high concentrations with air, permeation tubes and generation of the substance directly in an air stream. Monitoring systems are suggested to allow confirmation of the quantities generated. Details of construction are given.

17. KEY WORDS (Alphabetical order, separated by semicolons)

Gas mixtures; gas detectors; trace gas analysis.

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