GAS AND VAPOR GENERATING SYSTEMS
FOR LABORATORIES

by

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ABSTRACT

Systems used in the Monitoring Research Section's laboratory to
generate both static and dynamic concentrations of gases and vapors
for industrial hygiene sampling and analytical method development or
instrument evaluation are presented. The advantages and
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examples are included.

The equipment, apparatus, and calculations used in conjunction with
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TABLE OF CONTENTS

TABLE OF CONTENTS

INTRODUCTION

The Occupational Safety and Health Act of 1970 authorizes the Secretary of the Department of Health and Human Services to prescribe regulations requiring employers to measure, record and make reports on the exposure of employees to substances which may endanger their safety or health. The individuals responsible for making these measurements of exposure will often find it necessary to have available a reliable method for generating known concentrations of the substances they are required to measure, in order to calibrate the sampling instruments or verify the sampling methods used in the workplace.

The Monitoring Research Section of the Monitoring and Control Research Branch has been generating known concentrations of gases and vapors for many years [1,2], in order to develop or improve sampling and analytical methods and to evaluate the performance of portable pollution monitors used in the workplace. Because of the great variety of gases and vapors found in the workplace, no one method or system for generation could be applicable to all, yet all have some common components and some universal techniques. For the most part, equipment needed to generate known concentrations of gases and vapors is not commercially available as a complete unit, but must be assembled in the user's laboratory with components from various sources.

Several publications [3,4,5,6] have described one or more of the generation systems used in the Monitoring Research Section's laboratory, but these were brief and lacking in detail. The purpose of this report, therefore, is to describe, with as much detail as is practical, all the gas and vapor generation systems that have been used in this laboratory, so that the methods, equipment, and techniques which have evolved over the years will be available in summary form.

Basic Systems Used — Static and Dynamic

Two different systems are used to generate known concentrations of gases and vapors. They are static systems, or those that work by having an appropriate volume of contaminant gas or volatile liquid added to a known volume of air in a container; and dynamic systems, or those that work by blending a concentrated stream of contaminant gas or vapor with a dilution air stream to continuously produce a desired concentration.

Static Systems. Static generation systems used in the laboratory are usually containers with flexible walls (e.g. plastic bags) which can hold a volume of air. A sufficient quantity of the contaminant gas or volatile liquid is added to this air to make the desired concentration (Table 1). After allowing some time for the contents to come to equilibrium, samples may be taken from the bag or analytical instruments may be attached to it.

In addition to bags equipped with an air inlet port with an on-off valve and a septum, one needs a source of clean air, some means of metering it into the bag, and syringes for injecting the contaminant gas or volatile liquid.

For the most accurate statically generated concentrations, bags made of relatively inert materials (e.g. Tedlar, Teflon, Mylar) are commercially available or they may be fabricated by the user if the stock materials and sealing equipment is obtained (Table 2). It is necessary to carefully measure the volume of air and the quantity of volatile liquid or gas contaminant put into the bag if accurate and reproducible concentrations are needed. Tedlar or Mylar bags are most often used by this laboratory because they are heat-sealable, durable, and relatively inert materials. A dry test meter is used to measure the volume of air metered into the bag, and gas-tight syringes are used to add contaminant gases while microliter syringes are used to add contaminant liquids (Figure 1).

Occasionally, situations arise when an approximate concentration would be sufficient. For generating an approximate concentration, nothing more than a plastic bag with a tube secured in the opening is required. Air may be metered into it or the volume may be estimated and the required amount of contaminant added. This method cannot produce very accurate concentrations, but can be useful to help you determine rather quickly whether or not an instrument is responding to a particular substance and the approximate magnitude of response.

In addition to bags, rigid containers of glass, stainless steel, or plastic are useful for making known concentrations of gases and vapors. The advantages of rigid containers are that the volume does not have to be determined each time and there are fewer problems

with cross contamination, wall reaction, and leakage than with
flexible containers. The disadvantage is that only a small portion
of the total contents can be removed without changing the pressure
and thus changing the concentrations. This method is recommended
when only a small amount of a generated atmosphere is needed, (e.g.,
for injecting a few mL into a gas chromatograph for calibration).

Some advantages of static generation systems are their ease and
simplicity of use and the fact that the equipment needed is not
expensive to purchase. It is possible to make mixtures of two or
more contaminants in a single bag. Known concentrations may be
generated in the laboratory and then transported to a remote
location for calibrating an instrument.

The major disadvantage of statically generated concentrations is
that the volume of sample one can generate is limited by the size of
the bag available. Many substances with a TLV of 25 ppm or less
require sample volumes of 50 - 100 L in order to satisfy the
analytical method for that substance. It would, therefore, be
impossible to produce a statistically valid set of test data from a
single bag.

Also, with some substances, there can be interaction with the walls
of the bag. This will result in loss of the concentration with time
or, in some cases, a "memory" for the substance so that each time
the bag is filled with air the contaminant is generated anew.
Whenever these situations occur, the bag is no longer useful and
some other method of generation should be employed. Information on
the inertness of some of the bag materials is available (Table 3),
but for new substances not previously tested, some trial and error
may be required to determine whether or not it will be suitable for
a particular bag material.

For static generation systems, the primary limitation is the volume
of the container used, so the total volume needed for a particular
experiment or within a given time must be considered. Bags which
are purchased from stock sizes available from fabricators usually
range in size up to 90 - 100 L capacity. Larger sizes may be
fabricated on order or made in-house. Most rigid containers of
glass or stainless steel are of only a few liter capacity, yielding
only 10 - 20 mL useful volume per liter. Rigid plastic containers
of 20 - 30 L capacity have been used, but, for the more reactive
compounds, there could be a reaction with or loss upon the walls.
If large chambers made of stainless steel or glass are available,
these can be treated the same as smaller ones.

Dynamic Systems

Dynamic generation systems provide a continuous supply of the contaminant gas or vapor at a known concentration over a period of time. Normally, dynamic generation systems consist of two flowing streams of gas: the contaminant stream and the dilution air. By varying the relative amount of gas flowing in each stream, it is possible to generate a range of concentrations. These systems can produce the desired concentration continuously for up to several months if necessary, with only minor maintenance required. The total gas flow through a dynamic system will depend upon many factors, but the normal flow is between 1 - 12 Lpm. It is possible to produce mixtures of two or more contaminants with a dynamic generation system, and it is relatively easy to change from one contaminant to another. It is also possible, by installing other dilution air systems and mixing chambers, to produce proportionally lower concentrations of the generated substance simultaneously from the first concentration.

Dynamic Generation Systems - Components

The initial contaminant stream can be produced in several different ways, but the major components of a dynamic generation system are the same for each. These common components will be discussed first, followed by a discussion of the individual contaminant producing systems.

Two pieces of glassware, the mixing chamber and the sampling manifold, are necessary for all dynamic generation systems. Two other pieces of glassware, the liquid reservoir and the condenser, are necessary for some dynamic systems. Our laboratory uses some commercially available components for these as well as some custom fabricated parts (Figure 1).

The mixing chamber can vary in size and shape yet still perform its function, which is to receive the concentrated contaminant stream and the dilution air stream and mix them to provide a homogenous output to the sampling manifold. The mixing chamber our laboratory uses was fabricated from a long-neck, 1 L round bottom flask. An outlet port with an 18/9 ball and socket joint was installed in the bottom of the flask and a side-arm port was installed in the neck section to accommodate the second incoming gas stream (Figure 3). Two or more side arm ports may be installed to accommodate other contaminant streams if the production of a gas or vapor mixture is anticipated. All ports should have ball and socket joints in order to facilitate assembly and disassembly and to provide some flexibility to the system.

The sampling manifold's function is to provide a convenient place to sample the generated concentration, and its size and shape may vary

depending upon the user's needs. The sampling manifold our laboratory uses was fabricated from a 60 mm o.d. glass tube about 300 mm long. It has an inlet and outlet equipped with 18/9 ball and socket joints and seven sampling ports 4 mm i.d. along a plane. The sampling ports are about 30 mm long and 30 mm apart (Figure 2). This design facilitates the attachment of sampling devices to the manifold. Other designs could work just as well, and each user's needs will determine which design is best.

Seven sampling ports are suggested because it is often necessary to collect six samples simultaneously in order to validate a sampling method, and the seventh port is used to connect the sample line of the continuous monitor or other monitor or independent sampling method being used for verification of the concentration being produced.

Commercially available condensers (Allihn ball type 600 mm long with 35/25 ball and socket joints) are used, in conjunction with a constant temperature bath-circulator, for dynamic vapor pressure generation systems. These condensers can also be used with permeation tube generation systems if a commercially available permeation tube generation device is not available. These condensers may be installed either vertically or horizontally and maintain the outgoing contaminant gas stream of up to 100 mL at the set temperature of the circulated liquid. A glass thermometer or thermocouple may be installed near the exit of the condenser in order to monitor the temperature of the outgoing contaminant gas stream.

For vapor pressure generation systems, the condenser temperature is always maintained at least 2°C below ambient in order to prevent any further condensation of the vapors produced. For permeation tube generation systems the temperature may be above or below ambient, depending upon the permeation rates desired.

For vapor pressure generation systems, a reservoir is necessary to contain the liquid contaminant from which the vapor is produced. This reservoir is commercially available as a round bottom flask (250 - 1000 mL size) with a 35/25 ball and socket top fitting and a side arm port for introduction of the metered contaminant gas stream. A 12/5 ball and socket joint may be added to this side arm to facilitate disassembly, filling and cleaning. Impingers of bubblers may also be used in this capacity, singularly or in series (Figure 4a and 4b).

In many cases it is necessary to heat the liquid reservoir in order to assure saturation of the outgoing stream with the vapor being produced. Adding a heating mantle and power controller will allow the operator to maintain the reservoir at 35°C or whatever other elevated temperature is necessary to assure saturation of the stream.

In addition to these four basic parts, it is necessary to provide glass elbows and adaptors to facilitate convenient arrangement of the components, and a metal rod frame with clamps to support the assembly.

Using a dynamic generation system offers several advantages over static systems. Most obvious is the fact that the contaminant is continuously produced in the quantity needed, so that long term tests may be completed without interruption. Dynamic generation systems also provide the flexibility necessary to meet almost any requirements of concentration range from low ppb to high ppm. The same component may be used for vapor pressure generation, permeation and diffusion tube generation, syringe pump generation and gas mixture generation, with only small modifications or additions required to change from one system to another.

The major disadvantage of the dynamic generation system is the cost of the components. Also, a certain amount of laboratory bench space must be dedicated to this equipment. It is also necessary to provide a supply of clean air continuously, and this may require an additional investment for air cleaning equipment. The type of air cleaning equipment and the situations under which it is needed will be discussed later in this report.

Cylinder Dilution

For the generation of most gaseous contaminants, a relatively simple dynamic dilution system may be used. Cylinders of pure gases or mixtures are generally available, and these can be diluted to the desired concentrations so that with a single cylinder of a gas a range of concentrations may be generated (Figure 2). Dynamic generation systems for cylinder dilutions require some means to measure and control the contaminant and dilution air flow, plus a mixing chamber and sampling chamber. Static concentration may also be generated from gas cylinders by injecting or metering the required amount into a certain volume of air. See calculations (Table 1).

Permeation Tubes

For some gases, permeation tubes are available, and they offer some advantages over cylinders. This is especially true for corrosive or reactive gases which require special cylinders and regulators, and which may remain stable for relatively short periods of time. For these gases, e.g., Cl_2. NH_3, HF, NO_2, permeation tubes provide a source which is relatively safe and easy to handle and which will provide a stable output over a range of concentrations for up to several months.[8]

Complete permeation tube generation systems are available from manufacturers, or they may be assembled by individual laboratories. An example of a dynamic permeation tube generation system may be seen in Figure 3.

The rate of permeation of gas from a tube depends upon the length of the tube, the wall thickness, the temperature, and the permeability of the polymer tube (Table 4). For any given gas with a given tube dimension, the permeation rate, normally expressed as ng/cn/min, will remain constant after initial equilibrium as long as the temperature remains constant. Permeation tube manufacturers supply information necessary to determine the size and number of tubes needed for a particular application. A list of some permeation tube manufacturers may be seen in Table 5.

Permeation tubes may be calibrated by the manufacturer or they may be calibrated by the user if a microanalytical balance is available. The normal calibration procedure is to weigh the tube once per day over a period of several days while maintaining the tube at a constant temperature. When the recorded rate of weight loss becomes stable, the tube is ready to use, e.g., at equilibrium, and the weighing may be repeated thereafter on a weekly basis for as long as the temperature remains constant. The calibration procedure is necessary only if the exact permeation rate is needed. For a procedure requiring only an approximate concentration or where an independent analytical method is available to determine the exact concentration, the batch calibration provided by the manufacturer is satisfactory.[9]

Moisture in the air stream that is used to purge the permeated gas into the mixing chamber can adhere to the permeation tube and cause the permeation rate to change, so only dry air should be used. If dry air is not available or difficult to obtain, dry nitrogen is recommended since the total amount used is normally small in relation to the dilution air flow.

One disadvantage in using permeation tubes is the relatively large initial expenditure required to purchase the constant temperature device used; and this is especially true for systems which require maintaining the tubes at subambient temperatures and for user calibration if a microanalytical balance must be purchased.

Another is that the permeation rate is small for some compounds, so many tubes are required or the temperature must be elevated in order to obtain the desired contaminant level at the needed dilution air flow rate.

SYSTEMS USED FOR VAPORS

Dynamic Vapor Pressure Systems

There are several systems which may be used to generate known concentrations of vapors.[10] The system most often used in our laboratory is the dynamic vapor pressure generation system. Basically, this system consists of a reservoir of the contaminant liquid held at some elevated temperature, e.g., 35°C, over which a small stream of air or nitrogen is passed, e.g., 5 - 100 mL/min, into a tube type condenser maintained at some subambient temperature (Figure 4.a. & b.). Thus, the stream from the condenser is saturated with the contaminant vapor at the lower temperature. By knowing the vapor pressure of the substance at that temperature, it is possible to calculate the concentration in mole fraction of the substance in the stream (Table 6). Then it is possible to determine the exact amount of dilution air needed to produce the desired concentration of the substance (Table 7).

A dynamic vapor pressure generation system offers three variables which may be used to change the concentration: the contaminant stream flow rate, the dilution air flow rate, and the condenser temperature. Within certain limits, it is possible to produce a wide range of concentrations of many contaminant vapors. The limits for dilution air are: maximum; the amount available and the amount the mixing and sampling chambers can allow to pass through at approximately atmospheric pressure; and minimum, the smallest amount needed for the test or experiment. The limits for contaminant stream flow are: maximum; the greatest amount (normally about 100 mL/min) that can be passed through the condenser without changing the temperature; and minimum, the smallest amount that can be accurately measured. The limits for condenser temperature are: maximum; at least 2°C under ambient air and minimum, the lowest temperature at which the substance exhibits a vapor pressure and/or the lowest temperature that can be maintained without the coolant liquid freezing. For most situations it is easier to change the concentration by changing the dilution air flow rate than by changing the temperature because of the time required for the vapor to reach equilibrium after a temperature change.

Dynamic vapor pressure systems can be used for generating a wide range of concentrations (e.g., 1 - 1000 ppm) of most organic solvents and many other compounds (see Table 8).

Drawbacks to using this system include the cost of the subambient temperature control device and the fact that for some substances, vapor pressure information is difficult to find, or very limited,

(i.e., given for only one temperature) or in some cases incorrect or conflicting. Even so, this method is useful if an independent method is available to verify the generated concentration level, (i.e., gas chromatographic analysis based on external standards).

Syringe Pump Systems

Another useful method for generating known concentrations of vapors is by continuously injecting a volatile liquid into a flowing air stream using a variable speed syringe pump, or infusion pump (Figure 5). The injected liquid vaporizes in the flowing air stream, and by knowing the rate of injection and the amount of dilution air added, the contaminant concentration may be calculated (Table 9). It is necessary in some cases to heat the injection area in order to achieve complete vaporization of the liquid, while others will vaporize satisfactorily at room temperature. However, if a lot of heat is used to evaporate a relatively nonvolatile liquid, there may be a problem with condensation on the glassware if the room is cool or if the flow rate of air is low.

Since the output from the syringe pump and the volume of air added are the only variables, no constant temperature device is needed for this generation system. Otherwise, the same components used for a vapor pressure system may be used for this system.

Variable speed syringe pumps are available in different models, and those which offer the greatest range of pumping rates will provide the user with the versatility needed to cover a wide range of concentrations. In addition, the syringe size used can be selected from those of a few microliter capacity up to those of 20 mL capacity or greater. It is possible to inject as little as 1 uL per hour using a 10 uL syringe with the pump near its minimum setting.

The problem most often encountered with syringe injection systems is cyclic output, especially whenever the pump drive is operated in the lowest speed range with a microliter syringe. This problem is sometimes corrected by providing a larger than normal mixing chamber before the sampling chamber. For example, if the observed cycles occur every 4 minutes and the flow rate of the contaminant stream is 50 cc/min into a 500 mL mixing chamber located before the dilution air stream is added, the cycles can be eliminated by replacing the 500 mL mixing chamber with a 2 L mixing chamber or additional 500 mL chambers in series. This will provide sufficient residence time for the cycles to "smooth out" before the dilution air is introduced. Obviously, as the mixing chamber volume is increased, more time will be required for the stream to reach equilibrium.

Another means to reduce cyclic output from a syringe pump generation is to impale a small piece of felt fabric on the tip of the needle so that the liquid will flow out of the needle, spread out over the felt and evaporate more evenly. This may be used alone or in combination with larger mixing or surge chambers in difficult cases.

In addition to cyclic output, the other disadvantage to syringe pump systems is that the syringe must be refilled periodically, and this refilling operation can cause a disruption to the constant output level. It will, therefore, be to the user's advantage to carefully select the syringe size and pump speed so that refilling will come at the end of the predetermined sampling period rather than during the sampling period.

Diffusion Tube System

Diffusion tubes are a modification of the vapor pressure generation method, and may be used for many vapors, especially in the lower concentration ranges. The physical appearance of diffusion tubes may take many forms, but basically they consist of a reservoir containing the liquid and a capillary tube extending from above the liquid into a flowing stream of air (see Figure 6 - Diffusion Tube Generation System). At a constant temperature and a fixed tube length and diameter, the output of the vapor will be constant, and may be varied by changing the temperature of the reservoir or the length or diameter of the capillary tube. A constant temperature bath is ideal to control the temperature of the diffusion device. Room air or circulating tap water are satisfactory if their temperature is constant, or experiences only minor temperature fluctuations throughout the day.

As with other generation systems outlined here, it is better to pass a small stream of air across the diffusion device and then combine it with a dilution air stream in a mixing chamber. This will permit easy adjustment of the final concentration without disturbing the temperature or capillary length or diameter, and will minimize the cyclic output observed if the flow of air across the diffusion tube becomes large enough to cause uneven air currents or back-pressure.

Permeation tubes, previously discussed under Systems Used For Gases may also be used for vapor generation. The procedures to use and the equipment required are the same for both gases and vapors.

OTHER GENERATION SYSTEMS

Ozone is of concern to many in the industrial hygiene field and it is not covered by any of the previously described systems. Several ozone generators are commercially available which will produce stable concentrations of ozone in the range of interest to industrial hygiene (0.05 - 0.5 ppm) (Table 10). These systems

produce ozone by passing a controlled flow of air through a quartz tube which is irradiated by an ultraviolet light. The concentration of ozone produced can be controlled by varying either the intensity of the UV radiation reaching the quartz tube and/or by varying the flow of air through the quartz tube (see Figure 7, Ozone Generator Schematic).

Most commercial units will be supplied with a calibration curve from the manufacturer. The calibration should be checked periodically by an independent analytical method[7] in order to determine the actual ozone concentration for a given air flow rate and/or lamp shutter setting.

The U-Tube Generation System

The U-tube generation method can be used to load a sorbent tube with a known quantity of a specific contaminant in the vapor phase. This method is especially useful when an exact loading, but not an exact concentration, of some contaminant is needed to test a sorbent tube or other active sampling device.

In using this method, the sampling device is connected to a closed U-tube which may be modified by the addition of a septum port. The exact amount of liquid to be evaporated is injected into the tube and the sampling device is activated as the U-tube ports are opened. Sampling is complete when all the liquid is evaporated from the tube.

Obviously, this method must be used with caution because most hydrocarbons and halogenated compounds will evaporate rather quickly, often in one minute or less. This rapid evaporation could momentarily overwhelm the sorbent, causing loss of the sample and an erroneous determination of the true capacity of the sorbent for that particular substance.

Some control over the evaporation rate may be maintained by controlling the temperature of the U-tube either below or above ambient, although this method is normally used at ambient temperature and with substances that have relatively low vapor pressure.

Variations of this method may be used in individual situations. For example, a glass T with a septum will accomplish the same results as the U-tube when only a few microliters are to be evaporated at ambient temperatures. No calculations are necessary since the amount of substance evaporated is the amount absorbed by or loaded on the sorbent, except as noted above.

SYSTEMS USED IN CONJUNCTION WITH BASIC GENERATION SYSTEMS

Air Purification Systems

When a dynamic generation system is used, large quantities of clean air are required. It is usually impractical to supply this air by purchasing it in cylinders, but most facility compressed air supplies are contaminated with oil and water vapor and are subject to day-to-day variation depending upon ambient conditions. It is therefore recommended that air for the dynamic generation system be supplied by an air purification system, or a clean air generator.

The air purification system most often used by our laboratory is one which cleans up the in-house compressed air by removing most of the oil and water vapor. It consists of a series of components, beginning with an in-line cartridge containing a desiccant and molecular sieve which removes gross amounts of oil and water vapor, a small tube furnace operated at 1000 - 1200°F to burn the hydrocarbons to CO_2, a condenser coil to cool the air to ambient temperature, a charcoal filter to absorb any remaining organics, and a micron pore size pleated membrane filter to collect any particulates in the stream (Figure 8).

The pressure on the air line is maintained at about 15 psig by a pressure regulator at the inlet and this will provide about 25 Lpm at 6 - 8 psig at the outlet. A variable voltage controller is used to maintain the tube furnace at the desired temperature which is monitored by a thermocoupler readout meter (pyrometer) having an ANSI Type K thermocouple located near the outlet of the tube. The condenser coil is a jacketed tube through which a controlled amount (2-5 Lpm) of tap water is passed.

This system was assembled in our laboratory using available components, and requires periodic replacement of the various filters and regeneration of the charcoal bed. This system may also be used to clean ambient air supplied by a diaphragm, piston, or vane type laboratory air compressor.

Another system for cleaning facility compressed air has been used, and is similar to the system described above except that the tube inside the furnace is packed with a pelletized catalyst which will convert the hydrocarbons to CO_2. The temperature required to maintain the quality of the air is 300 - 400°C depending upon the quantity of air needed and the size of the catalyst bed. This temperature may be determined experimentally by monitoring the output with a hydrocarbon analyzer.

-12-

If the ambient air in the laboratory is relatively clean and not
subject to outside contamination or day-to-day fluctuations, a
simple system consisting of an oil-less compressor followed by a
charcoal trap and a particulate filter may be all that is needed to
produce air of satisfactory quality for most experiments.
Commercial pure air generators are also available and have been used
in our laboratory (see Table 11). These devices are compact and
require little maintenance. Various sizes are available to provide
the quantity of air needed.

The air purification system that one chooses will depend upon the
quantity of air expected to be used, the availability and quality of
house air, space availability, the amount of money available to
invest, and the type and concentration of gas or vapor to be
generated.

The air produced by any of the above methods may contain some
impurities, but it will be within acceptable limits for the majority
of applications and it will be consistent over a long period of time.

Humidity Generation, Control, and Measurement

Air from most air purification systems is normally dry, (i.e.
10% RH) so it is necessary to add water vapor to the dilution air
stream in order to produce concentrations of gases and vapors with a
realistic relative humidity range, and to test methods over a range
of humidities. Since realistic range may vary between 10% and 80%
or more relative humidity, it is necessary to be able to control and
measure the amount of water vapor added.

A very simple system for generating humidity in the air has been
used by our laboratory for several years and has proven to be
reliable and consistent. This system consists of a container of
water over which varying amounts of the dilution air stream may be
passed (see Figure 8). The air stream is split and 2 control valves
are installed, making it possible to pass as much or as little of
the air across the water as is necessary to produce the desired
relative humidity.

Depending upon the air flow rate and the humidity level desired,
additional containers may be added and/or the water may be heated in
order to increase the amount of water vapor available. Because of
condensation, heating makes it more difficult to control the level
of humidity, and should be used as a last resort. This system
eliminates the problems caused by varying pressure drop and
entrainment of water droplets associated with those systems which
require bubbling the air through water.

-13-

Measurement of the generated water vapor will usually be necessary.
This may be done by a wet-bulb thermometer or by one of several
commercially available electronic humidity sensor-readout devices
(Table 12). The wet-bulb thermometer technique is satisfactory if
only an approximate or occasional check of the relative humidity is
needed, whereas the electronic sensor is necessary for the most
accurate continuous readout and if it is desirable to have a
permanent record of the humidity level for a given time.

Concentration Monitoring Systems

An independent monitor is necessary to determine the actual
concentration of the gas or vapor being produced. The selection of
a monitor or independent sampling method to use will depend upon
many factors including the kind of gas or vapor being generated, the
concentration level, and if it is a single component or a mixture.
In general, monitors may be classified as continuous or
intermittent, and these may be further classified as specific or
non-specific.

Continuous monitors are those whose sample lines are attached
directly to the generation system sample manifold and provide a
continuous direct readout and/or a permanent record of the
concentration level at any time during the operation. Continuous
monitors include non-specific instruments such as flame ionization
detectors, photoionization detectors and infrared detectors and
specific instruments such as CO detectors, mercury vapor detectors,
and NO/NO_2 detectors (Table 13). Continuous monitors are most
useful where only a single contaminant is present to be measured, as
would be the case whenever a sampling method or procedure was being
evaluated. However, continuous monitors may also be useful for
monitoring mixtures, either alone or in combination with one or more
other continuous monitors, in certain situations.

Intermittent monitors are instruments or devices which can be used
to measure the concentration level at intervals throughout the
operation, either directly, as is the case when a gas chromatograph
with an automatic gas sampling valve is attached to the sample
manifold; or indirectly, as when a series of sorbent tubes or
sorbent solution samples are collected throughout the sampling
period and later analyzed.

Flame ionization detectors will respond to almost all hydrocarbons,
and have been used by our laboratory more than any other instrument
for monitoring the concentration of generated gases and vapors.
Flame ionization detectors are durable, reliable, simple to operate
and require very little maintenance. Depending upon the model
chosen, they are able to monitor a wide range of concentrations.

Photoionization detectors will respond to a wide variety of organic compounds and some inorganic compounds. The range of concentrations that can be monitored include most that would be encountered in industrial hygiene monitoring situations. This detector, although relatively new, has been found to be durable, reliable, simple to operate, and relatively maintenance free.

Infrared analyzers may be used to monitor a single contaminant continuously or may be used to monitor mixtures of contaminants intermittently. Many contaminants have characteristic absorption bands in the infrared region of the spectrum, and the amount of infrared radiation absorbed by a sample can be directly related to the concentration of the contaminant. Some infrared analyzers are equipped with a specific wavelength filter and can be used for that substance only, while some have a variable wavelength guide and will monitor for several components by scanning the spectrum.

Although less frequently used in this laboratory, UV visible absorption monitors with long path cells are available to monitor some contaminants.

Chemiluminescent detector systems for ozone, ammonia and oxides of nitrogen are available and are used by this laboratory. This detector principle has been found to be accurate and stable and is especially useful when monitoring very low levels of these contaminants.

Other monitoring systems are available for both specific and general applications. The choice of which system to use for a particular application depends upon many considerations: availability, cost, range and level of response, accuracy, ease of operation, frequency of use - to mention a few. Also important to consider is the required sample flow rate into the monitor when the generation system is set up. While most monitoring systems function quite satisfactorily with a sample flow rate of 1 Lpm or less, some may require up to 5 Lpm or more, which would seriously limit the usefulness of a concentration generation system designed to produce only 4 Lpm total flow, for example.

Air Flow Rate Measurement and Control

The importance of measuring and controlling the quantity of air flowing in a generation system cannot be overemphasized. Small variations or errors in air flow can produce larger errors in the final concentration of contaminant produced. Knowing the exact amount of air placed in a static system is also very important to both the accuracy and reproducibility of the concentration.

Several methods and devices for measuring air flow are currently in use. Each has some advantages and some shortcomings, but by careful selection and application of these various methods, it is possible to maintain the exact amount of air that is needed.

Any flow measurement device must be calibrated before use in order to assure its accuracy. The most convenient method for calibrating flow measuring devices is the soap film flow meter, or bubble meter as it is sometimes known. These operate by permitting the air stream to force a soap (film) bubble through a calibrated glass tube. The time required for the soap film to travel through a certain volume in the tube is an accurate measure of the air flow rate. This is a primary standard by which other measurement devices may be calibrated (Figure 9).

Soap film flow meters may be assembled in the laboratory, using Class A burets which are usually available in any laboratory, or they may be obtained in kits which include a stand and other necessary components. For convenience, at least 2 sizes should be obtained: small (100 mL) size for flow rates of 500 mL/min or less, and a large (1 - 2 L) size for flow rates up to 10,000 mL/min. Other sizes are available but these will be adequate for most situations. Soap film flow meters may be used to measure a stream of air under vacuum or with positive pressure. For measuring streams with positive pressure, the soap solution is placed in a rubber bulb and the air enters by a side port whereas for streams under vacuum the tube is inverted and the soap solution is held in a beaker (see Figure 9). Soap film flow meters are also useful for calibrating sampling devices so that the total volume sampled may be determined very accurately. In addition to the buret and soap solution, a stopwatch is necessary and a small calculator is very useful and time saving, especially in situations where the flow rate is being adjusted to a given level.

Secondary standards, such as wet test meters or dry test meters, are very useful devices for accurately measuring the flow rate of an air stream or for measuring the total amount of air going into a static system. Wet test meters must be leveled and the water level checked frequently. For those meters equipped with a manometer for measuring the pressure drop across the meter, the manometer must be checked periodically for fluid level. For both wet and dry meters, it is important never to exceed the flow rate or pressure drop specified by the manufacturer. If a wet test meter is used to measure the air going into a system where dry air is desired, a desiccant cartridge should be placed after the meter because the air passing through the meter will collect some moisture, the amount depending upon the temperature, humidity, and flow rate of the incoming stream. Both wet and dry test meters should be calibrated periodically with a soap-film flow meter.

Rotameters are frequently used to measure and monitor the flow rate of air. They are relatively inexpensive and are available to cover an almost infinite range of flow rates. For flow rates of less than 200 mL/min however, rotameters have been found to provide only marginal performance even when calibrated frequently. For greater flow rates, performance is satisfactory, provided that the incoming air is free of particles or oil mist which could become attached to the float or walls of the tube, thus changing its calibration. For applications requiring absolute measurement of the air flow, rotameters should be used only as indicators of flow and not primary flow measurement devices unless the air is clean and dry, the pressure carefully controlled, the temperature constant and the calibration checked each time the flow rate is changed.

Electronic mass flow meters are available in a wide range of flow rates and have been found to be especially useful in the low flow rate range (500 mL/min and less) where the performance of rotameters is marginal.

Mass flow meters are expensive, but may prove to be a good investment since they are capable of accurately measuring extremely low flow rates and are not affected by normal variations in ambient temperature and pressure. The flow sensor may be located in a remote area, while the readout can be conveniently placed near the operator. Most mass flow meters are available with recorder output so that a permanent record of the flow rate may be provided. Mass flow meters should be individually calibrated with the gas (air, N_2, etc.) to be used and under the same conditions (temperature, pressure) as they will be used (Table 14).

Another very useful device for measuring gas flow is the calibrated orifice. There are two basic conditions under which the orifice can be used: critical and limiting (see Figure 10). The critical orifice is used primarily when a single flow rate is needed. Critical flow is obtained by applying critical pressure to one side; that is, the pressure drop across the orifice is 0.5 atmospheres or greater. Under this condition, the flow rate through the orifice varies directly with any pressure drop ahead of the orifice (i.e, sampling devices). Critical orifices are often used for laboratory sampling when several samples are collected simultaneously. It is possible to obtain orifices from manufacturers in a variety of sizes or they may be made in the laboratory if the material and equipment is available (Table 15).

Limiting orifices are the same as critical orifices in appearance, but are used at lower pressures as flow restrictors. Under a given set of conditions, i.e., ∇ P ahead of the orifice and pressure to or from the orifice, reproducible flow is obtained (Figure 10).

A needle valve or other fine metering valve may be used as a variable limiting orifice or as a critical orifice if precautions are taken to prevent the stem from moving from its set position. Any vibration or motion in the area of the valve should be avoided. Because of the small opening in any orifice, care must be exercised to keep dust from entering to change or stop the flow.

When using an orifice to measure or control the flow rate, it is necessary to provide a means of indicating the amount of pressure drop across the orifice and ahead of the orifice. For lower pressure measurements, the most satisfactory means to measure it is with a manometer. Manometers which are designed to read pressures in inches of water are available which can detect changes in pressure as small as 0.01" H_2O (Table 16). Manometers may also be used to monitor the pressure inside a generation system, which should be maintained at just above (0.1 - 0.8" H_2O) atmospheric pressure.

In addition to manometers, there are diaphragm activated gauges available which are capable of measuring a wide range of pressures including the low inches of water range. These gauges provide a direct readout on a dial, and may be permanently mounted in a panel if desired. This type gauge can also be electronically activated and coupled with a flow controller to provide unattended compensation for line pressure changes.

Temperature - Measurement and Control

For generation systems utilizing the vapor pressure of a liquid or permeating tube, it is necessary to be able to measure and provide control of the temperature within close tolerances ($\pm$ 0.2°C) in order to obtain a uniform output of the contaminant.

Many devices are available which will provide the controlled level of power necessary for those systems which operate at above ambient temperatures. For example, heating mantles for flasks, controlled by a variable autotransformer, will provide a constant elevated temperature for liquids in glass containers. Also, hot plates, heating tapes, strip heaters and immersion heaters may be used so long as adequate control is provided. Some experimentation will be necessary to determine the voltage required to maintain a certain temperature in a vessel or circulating bath, but once this is established the temperature will remain constant. The different heating devices and variable autotransformers are available from most laboratory supply houses at rather modest cost (see Table 17). Systems which must operate at subambient temperatures should be purchased as a unit for best results. Constant temperature

bath-circulators equipped with heaters and refrigeration units are available and will provide a controlled environment in the range of $-20°$ to $+70°C$ (Table 18). While these devices represent a substantial investment, they are almost indispensable for generating very low concentrations of substances which have a high vapor pressure. The reservoir on these baths may be used directly or the liquid may be circulated through jacketed vessels to provide the controlled temperature in a remote area.

Temperature measurement may be done in several different ways, depending upon the temperature range measured, the degree of accuracy and readability required, and whether or not controllers and/or recorders are needed. Three basic types of temperature measurement devices are generally available: liquid in glass, bimetallic dial type, and electronic.

Glass thermometers may be used for most applications up to about $400°C$. Accuracy is easy to determine by ice bath or by boiling water and readability may be as good as $\pm 0.1°C$ or better, depending upon the scale selected. Most laboratory supply houses offer a variety of glass thermometers in ranges to cover most applications.

For situations where there is a possibility of the glass thermometer being broken or where readability is a problem, metal thermometers using a bimetallic sensor and a dial readout are a good choice. Their range is up to $400°C$ and their accuracy is $\pm 1\%$ full scale for most models although some are accurate to $\pm 0.5\%$ full scale. Bimetallic dial type thermometers are readable to within $\pm 0.05°C$ and, depending upon the size dial selected, may be readable from several feet away. These thermometers are also available from most laboratory supply houses.

For higher temperatures, for remote monitoring, or for controlling and/or recording temperature, electronic devices such as thermocouples or thermistors with the appropriate readout device are available. The cost of electronic temperature devices range from modest to expensive. For example, a single thermocouple readout meter may be obtained for about $50, whereas a digital meter capable of reading several thermocouples and with recording capability may cost several hundred dollars. The unit chosen will depend upon the user's needs and resources. Thermocouples capable of measuring temperatures up to $800°C$ or higher are available from laboratory supply houses or directly from the manufacturer.

Laboratory Ventilation and Safety Considerations

Before any gas or vapor generation system is installed in the laboratory, provisions must be made for venting the unused gases out

of the room. In some situations, it is best to have the entire
generation system installed in a laboratory fume hood, while in
other situations it may be necessary to vent only the exit port of
the generation system after making sure there are no leaks in the
generation system. It will be necessary to make a determination of
the potential hazards of each substance generated, based on its
known or assumed properties.

As with any work area, it is desirable to have good air circulation
in the laboratory and a constant, comfortable temperature, both from
the standpoint of worker comfort and for the operation of precision
laboratory instruments, some of which may produce erroneous readings
if there are wide fluctuations in the ambient temperature.

SUMMARY

Gas and vapor generation systems are valuable tools for many
applications, including the evaluation of the performance of
sampling methods and sampling instruments.

With the exception of some permeation tube and diffusion tube
devices, pre-assembled generation systems are not commercially
available, and must therefore be assembled by the individual user.
The installation may range from very simple, inexpensive, and rigid
systems up to complicated, expensive and versatile systems. The
system installed will depend upon many factors, and each should be
considered before any investment is made (TABLE 19).

Experience has shown that the greatest single source of error in any
generation system is in the measurement and control of the air flow
rate. Therefore, emphasis should be placed on this aspect by
obtaining the best in air flow measurement and control devices that
can be afforded and by becoming proficient in their operation and
calibration.

The basic components of dynamic generation systems are air supply,
air control and measurement, mixing chamber and sampling chamber or
manifold. Each is used with vapor pressure, permeation tube, or
syringe pump generation systems. By designing these with some
flexibility, it will be easy to install a different system if the
first one no longer meets the needs of the laboratory.

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   Intersociety Committee
   R.R. Donnely & Sons Co.
   Crawfordsville, IN
   L cc No. 77-6826 pp. 16-26

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22

TABLE 1

Static Concentration Calculations

Static concentrations of contaminant gases and vapors are generated by introducing a known volume or weight of the contaminant into a known volume of air or other dilution gas.

A. For a gas the concentration is calculated in a straightforward manner

$$\frac{V_c}{V_d} = C$$

where

V_c is the quantity of the contaminant

V_d is the volume of the dilution gas

C is the concentration of the contaminant in the dilution gas

The units of V_c, V_d and C may vary.

Some common examples are:

$V_c = \mu L$, $V_d = L$; $C = \mu L/L$ or ppm

If C is to be given in units of mg/m^3, the V_d must be given in M^3 and V_c must be given in mg. This can be accomplished in either of two calculations:

TABLE 1 (cont'd.)

Static Concentration Calculations

1. Convert the volume of the contaminant gas to mg:

    e.g. convert ul to mg

    $$\frac{V_c \times MW_c \times 10^3}{\overline{V} \times 10^6} = W_c$$

    where: W_c = Weight of contaminant in mg.

    V_c = Volume of contaminant in uL

    $\overline{V}$ = Molar volume in liter/mole

    MW_c= Molecular weight of the contaminant in grams/mole

    10^3= Conversion factor mg/gm

    10^6= Conversion factor uL/L

    This equation can be reduced to

    $$\frac{V_c \times MW_c}{\overline{V} \times 10^3} = W_c$$

2. A direct conversion of ppm to mg/M³:

    $$C_m = \frac{C_p \times MW_c \times P_s \times T_o}{\overline{V} \times P_o \times T_s}$$

    $$C_m = \text{conc. in mg/m}^3$$

TABLE 1 (cont'd.)

Static Concentration Calculations

$$C_p = \text{Conc. in ppm (uL/L)}$$

$$MW_c = \text{Molecular weight of the contaminant}$$

$$P_s = \text{Pressure of the air sampled in mm Hg}$$

$$T_o = \text{Standard Temperature in } {}^{\circ}K$$

$$\bar{V} = \text{Molar Volume in liters/mole}$$

$$P_o = \text{Standard pressure in mm Hg}$$

$$T_s = \text{Temperature of sample air in } {}^{\circ}K$$

B. For a <u>Vapor</u> the volume of gaseous sample generated from a given liquid volume must be calculated.

This can be done using:

$$V_g = \frac{V_1 \times d \times \bar{V} \times P_o \times T \times 10^3}{MW_c \times P \times T_o}$$

where:

$$V_g = \text{Gaseous volume of contaminant in mL}$$

$$V_1 = \text{Liquid volume of contaminant in mL}$$

$$d = \text{Density of contaminant in gm/mL}$$

$$\bar{V} = \text{Molar volume at temperature, T in liter/mole}$$

$$P_o = \text{Standard pressured in mm Hg.}$$

$$T = \text{Temperature of contaminant/system, } {}^{\circ}K$$

TABLE 1 (cont'd.)

Static Concentration Calculations

10^3 = Conversion factor, mL/L

MW_c = Molecular weight of contaminant, gms/mole

P = Pressure of contaminant/system, mm Hg

T_o = Standard temperature, °K

Once the gaseous volume of the vapor is known, it can be treated the same as a gas.

As an example, in order to make a bag of 500 ppm methylene chloride (CH_2Cl_2) the following facts are found: density of methylene chloride, 1.3255 g/mL; molecular weight, 84.94; ambient temperature 24°C, ambient pressure, 745 mm Hg. In addition, some volume of liquid to use must be assumed, normally 1 - 100 ug (0.001 - 0.1 mL) depending upon the size of the static container and the concentration desired. Then apply these numbers to the above formula.

$$Vg = \frac{0.05 \text{ mL} \times 1.3255 \text{ g/mL} \times 24.45 \text{ L/mole} \times 769 \text{ Torr} \times 298° \times 10^3 \text{ mL}}{84.94 \text{ g/mole} \times 745 \text{ Torr} \times 298°K}$$

Vg = 19.46 mL gas

Thus, 0.05 mL (50 uL) methylene chloride liquid will produce 19.46 mL methylene chloride vapor at room temperature. Next, determine how much air will be needed in the bag to produce a concentration of 500 ppm.

$$V_d = \frac{V_c}{C}$$

$$V_d = \frac{19460 \text{ μL}}{500 \text{ ppm}}$$

$$V_d = 38.92 \text{ L}$$

If the other concentrations or different volumes are needed, it is necessary to change the volume of liquid used, or to make an additional dilution of the original concentration.

TABLE 1 (cont'd.)

Static Concentration Calculations

If further dilution of the static concentration is required, three pieces of information are required.

1. The concentration of the contaminant gas as determined by one of the above methods, C_o

2. The volume of the contaminant gas that is drawn from its container, V_c

3. The volume of additional dilution air, V_a

The new concentration is handled in a straightforward manner:

$$\frac{V_c \times C_o}{V_c + V_a} = C_n$$

Where C_n is the new concentration of contaminant. C_n has the same units as C_o.

TABLE 2

Sources of Gas Sample Bags

Pollution Measurement Corp.
P.O. Box 6182
Chicago, Illinois 60680

Environmental Measurements Inc.
215 Leidesdorff Street
San Francisco, California 94111

Fluorodynamics Inc.
Diamond State Industrial Park
Newark, Delaware 14711

Lapine Science Corporation
6001 South Knox Avenue
Chicago, Illinois 60629

The Anspec Company Inc.
P.O. Box 7044
Ann Arbor, Michigan 48107

NASCO
901 Janesville Avenue
Ft. Atkinson, Wisconsin 53538

Calibrated Instruments Inc.
731 Saw Mill River Road
Ardsley, New York 10502

Polyfoam Packers Corporation
6415 North California Avenue
Chicago, Illinois 60645

Analabs, Inc
80 Republic Drive
New Haven, Connecticut 06473

Scientific Gases & Instruments
P.O. Box 6
Houston, Texas 77001

Cole-Parmer Instrument Company
7425 North Oark Park Avenue
Chicago, Illinois 60648

Varian Instrument Service Center
670 East Arques
Sunnyvale, California 94806

TABLE 3

Sources of Information about Bag Material

Teflon - Tedlar - Mylar:

E.I. DuPont De Nemours and Company (Inc.)
Film Department
Wilmington, Delaware 19898

Scotch - Pac:

3M Company
3M Center
St. Paul, Minnesota 55101

TABLE 4

Calculations for Permeation Tube Generation Systems

Permeation Tubes can be used to generate concentrations of
contaminant gases and vapors due to the permeability of fluorocarbon
resins to these gases and vapors.[8] The degree of permeability
is given by the permeability coefficient P.

$$P = \frac{W_c \times T_f}{A_f \times T_c \times P}$$

where W_c =   weight of the permeating contaminant

T_f =   film thickness

A_c =   area of film

T_c =   contact time

P =   pressure difference

The permeation (or diffusion) of the contaminant gas or vapor
increases non-linearly with temperature, pressure and surface
contact area. The permeation decreases with the wall thickness of
the tube and the density of the fluorocarbon resin used to make the
tube.

To calculate the concentration of contaminant from the permeation
tube, the permeation rate, expressed in ng/cm/min, of the
contaminant must be known. This information can be obtained in two
ways:

1)   from the manufacturer's calibration

2)   self - calibration. -- After a 2 - 5 day equilibration
      period in the constant temperature oven, the permeation
      tube should be weighed in a periodic manner, at preferable
      constant time intervals. The key here is to maintain the
      permeation tube at a given temperature. A plot of weight
      versus time should be linear and the slope of the line will
      be the permeation rate.

Once the permeation rate is accurately known, the concentration that
is generated is given by:

TABLE 4 (cont.'d.)

Calculations for Permeation Tube Generation Systems

$$C_p = \frac{R_p \cdot L}{F_d}$$

where C_p =   concentration, permeation tube (ng/L)

R_p =   permeation rate (ng/cm/min)

L =   length of permeation tube (cm)

F_d =   flow rate of dilution gas (L/min)

Obviously, the concentration is convertible to any desired units by employing the appropriate conversion factors.

Beside using the above calculation to determine the concentration generated by the permeation tube at a given temperature and volume of dilution gas, it is often wise, always recommended and sometimes necessary to determine the concentration using some independent, accurate and reliable analytical technique.

If further dilution of the contaminant stream is needed, three pieces of information must be recorded:

1.   the concentration of the first-stage of the contaminant stream, C_p

2.   the rate, R_{cp} at which the contaminant stream with concentration C_p is being pumped into the second dilution chamber and

3.   the flow rate volume of the additional dilution air. F_{d2}

Then

$$C_n = \frac{C_p \times R_{cp}}{R_{cp} + F_{d2}}$$

Calculations for Permeation Tube Generation Systems

where C_p =   concentration   ng/L

R_{cp} =   contaminant stream flow rate   L/m

F_{d2} =   flow rate of dilution gas   L/m

C_n =   (new) desired concentration   ng/L

TABLE 5

Sources of Permeation Tubes

Analytical Instruments Development, Inc.
250 South Franklin Street
West Chester, Pennsylvania 19380

Metronics Associates, Inc.
3201 Porter Drive
Stanford Industrial Park
Palo Alto, California 94304

Tracor Instruments
Tracor Incorporated
6500 Tracor Lane,
Austin, Texas 78721

Varian Instrument Service Center
670 East Arques
Sunnyvale, California 94086

TABLE 6

Sources of Vapor Pressure Information

Vapor Pressure of Organic Compounds
T. Earl Jordan
Interscience Publishers, Inc.
250 5th Avenue
New York, New York
52-11414

The Vapor Pressure of Pure Substances
T. Boublik, V. Fried, E. Hola
American Elservier Publishing Company
52 Vanderbilt Avenue
New York, New York 10017
72-97420

Handbook of Chemistry and Physics
Robert C. Weast, Editor
Chemical Rubber Company Press
18901 Cranwood Parkway
Cleveland, Ohio 44128
13-11506
Section D., pp. 162-188

TABLE 7

Calculations for Vapor Pressure Generation

Dynamic concentrations of vapors may be calculated if the vapor pressure at a given temperature of the species of interest is known.

Initially, the concentration of the contaminant stream must be determined. The liquid, from which the vapor is generated, is warmed (usually in a round-bottom flask in a heating mantle) to some above ambient temperature (32° - $36^\circ C$). A small stream (known flow rate) of air or other matrix gas is passed over the liquid, resulting in the air stream becoming saturated with the vapor. This stream then passes through a condenser held at a constant, known subambient temperature at which the vapor pressure of the contaminant liquid is accurately known, and at which its concentration can be determined in mole fraction, since –

$$C_{mf} = \frac{P_v}{P_a}$$

where
C_{mf} = concentration of the vapor in mole fraction

P_v = vapor pressure of the contaminant at the experimental temperature, mm Hg

P_a = ambient barometric pressure, mm Hg

The necessary flow of dilution air, F_d, needed to give the final desired concentration, can be calculated from the mole fraction (above calculation) and the desired concentration of vapor in the final contaminant stream.

$$F_d = \frac{F_c \times C_{mf} \times 1000}{C_d} - F_c$$

where

F_d = flow rate of dilution air (L/min)

F_c = flow rate of contaminant stream (mL/min)

C_{mf} = concentration in mole fraction (unitless)

C_d = desired final concentration, ppm (μL/L)

1000 = conversion factor (μL/mL)

TABLE 7 cont'd.)

Calculations for Vapor Pressure Generation

The F_c flow rate is the stream of air or the other matrix gas that
is passed over the round-bottom flask, through the condenser, and
into the mixing chamber. The value of F_c is set at some nominal
value (e.g., 50 mL/min) before calculation of the flow rate of the
dilution air, F_d. Also, determine the ambient barometric pressure
for these calculations, 745 mm Hg is used because it is a typical
barometric pressure for this area.

Sample Calculations: Assume a concentration of 100 ppm styrene is
needed. The vapor pressure of styrene is 5.6 mm Hg at 20°C, and
for the initial calculation a contaminant stream flow of 50 mL/min
is assumed. First, the concentration in mole fraction is calculated.

$$C_{mf} = \frac{P_v}{P_a}$$

$$C_{mf} = \frac{5.6}{745}$$

$$C_{mf} = .0075$$

Then, the amount of dilution air needed to achieve the 100 ppm
concentration is calculated.

$$F_d = \frac{F_c \times C_{mf} \times 1000}{C_d} - F_c$$

$$F_d = \frac{50 \times .0075 \times 1000}{100} - 50$$

$$F_d = 3.70 \text{ L/min}$$

Thus, with a 50 mL/min contaminant stream flow through the condenser
held at 20°C, the addition of 3.70 L/min dilution air to the
mixing chamber will produce a concentration of 100 ppm at the
sampling manifold.

If other concentrations are needed, then it is necessary to change
only the dilution air flow or the contaminant stream flow.

TABLE 7 (cont.d)

Calculations for Vapor Pressure Generation

For substances which have a high vapor pressure, a second dilution
of the first concentration may be necessary in order to produce a
low concentration. Acetone, for example, has a vapor pressure of
175 mm Hg at 20° and 112 mm Hg at 10°C. It is immediately
apparent that the amount of dilution air necessary to produce a
concentration of 100 ppm acetone will be great, and perhaps more
than the system can handle, at ambient pressures, even if the
condenser temperature is reduced at 10°C.

$$C_{mf} = \frac{112}{745} = .150$$

$$F_d = \frac{50 \times .150 \times 1000}{100} - 50 = 74.95 \text{ L/min}$$

At this point, two approaches may be taken. First, the contaminant
stream flow, F_c, may be reduced to 5 mL/min. This would reduce
the amount of dilution air needed to 7.5 L/min which is reasonable.
The second approach is to increase the concentration produced to
1000 ppm and then take a stream from this concentration into a
second mixing chamber where additional dilution air is added to
produce the desired new concentration.

$$F_{d2} = \frac{C_d \times R_{cd}}{C_n}$$

where

C_n is the new concentration

C_d is the first concentration

R_{cd} is the rate at which the contaminant C_d is
being pumped into the second dilution chamber.
L/min (assumed)

F_{d2} is the flow rate of the second dilution air
stream. L/min.

TABLE 7 (cont'd.)

Calculations for Vapor Pressure Generation

Thus, by adjusting R_{cd}, the final concentration, C_n, can be produced with a manageable amount of dilution air.

$$F_{d2} = \frac{C_d \times R_{cd}}{C_n} - R_{cd}$$

$$F_{d2} = \frac{1000 \times 50 - 50}{100}$$

$$= 50 \frac{mL}{min} \left(\frac{1000 \text{ ppm}}{100 \text{ ppm}} - 1 \right)$$

$$F_{d2} = 450 \text{ mL/min}$$

This calculation is also used for generating dynamic concentrations from cylinders or bags containing known, higher concentrations.

TABLE 8

List of Some Substances Generated by the
Vapor Pressure Method and Range of Concentrations

Substances Generated	Concentrations, ppm
Trichloroethylene	10 – 300
Methylene Chloride	25 – 250
Toluene	25 – 300
Acetone	25 – 1000
Hexane	250 – 2000
PCB's	0.5 – 10
Styrene	25 – 200
Benzene	10 – 200
MEK	25 – 500
Epichlorohydrin	1 – 25
Trichloronitromethane	0.1 – 10
DBCP	0.01 – 10
2-Nitropropane	1 – 10
Carbon Disulfide	5 – 50
Methyl Alcohol	50 – 400
Mercury	0.5 – .5 (mg/m^3)

TABLE 9

Syringe Pump Generation Calculations

In order to determine the liquid flow (from the syringe) necessary to generate a given gaseous concentration use

$$F_1 = \frac{C_d \times F_d \times MW_c}{\overline{V} \times d \times 10^3}$$

where

F_1 = the liquid flow required (uL/min)

C_d = desired concentration in ppm (uL/L)

F_d = flow rate of the dilution air (L/min)

MW_c = molecular weight of the contaminant (g/mole)

$\overline{V}$ = molar volume (25 L/mole at 745 mm Hg and 25°C)

d = liquid density of the contaminant (g/mL)

It is important to point out that F_d includes the small stream of air or other matrix gas that carries the contaminant vapor into the main stream in addition to the bulk dilution air or other matrix gas.

Once the necessary liquid flow has been determined, it is necessary to select an appropriate syringe and the proper operating settings for a given syringe pump. The choice of syringe and pump settings is a function of the required liquid flow and the sampling time desired. Always bear in mind that instruments generally function most accurately when they are operated in the 30 - 70% full scale range.

The volume of the vapor produced by the evaporation of the liquid is small compared to the total air volume of the contaminant and dilution air streams. Example: To generate 1000 ppm Hexane at 1 L/m dilution air.

$$F_i = \frac{1000 \text{ ppm} \times 1 \text{ LPM} \times 86.2 \text{ g/mole}}{25.0 \text{ L/mole} \times 0.66 \text{ g/mL} \times 10^3}$$

$$= 5.23 \text{ ul hexane liquid/min}$$

The volume of 5.23 µL hexane when vaporized is:

$$V_R - 5.23 \frac{ML}{Min} \times 10^{-3} \frac{\mu L}{\mu L} \times 0.66 \text{ g/mL} \times \frac{1 \text{ mole}}{86.2 \text{ g}} \times \frac{25.0 \text{ L}}{\text{mole}} = .001 \text{ L/min}$$

Therefore, the final concentration of hexane produced is:

$$1000 \text{ ppm} \times \frac{1.0 \text{ L/min}}{(1.0 + 0.001) \text{ L/min}} = 999 \text{ ppm}$$

TABLE 10

Manufacturers of Ozone Generators

Cole Parmer Instrument Company
7425 North Oak Park Avenue
Chicago, Illinois 60648

Columbia Scientific Industries
P.O. Box 9908
Austin, Texas 78766

Ultra-Violet Products, Inc.
5100 North Walnut Grove Avenue
San Gabriel, California 91778

Atlantic Vetraviolet Corporation
250 North Fehu Way
Bay Shore, New York 11706

Dasibi Environment Corporation
616 East Colorado Street
Glendale, California 91205

Horizon Ecology Company
9435 North Oak Park Avenue
Chicago, Illinois 60648

TABLE 11

Some Sources of Air Cleaning Equipment

Aadco, Inc.
2257 Lewis Avenue
Rockville, Maryland 20852

Bolston, Inc.
Box C
703 Massachusetts A
Lexington, Massachusetts 02173

Puregas Heatless Air Drier
Curtin Matheson Scientific
4220 Jefferson Avenue
P.O. Box 1546
Houston, Texas 77001

Matheson Gas Products
P.O. Box 85
932 Patterson Plank Road
East Rutherford, New Jersey 07073

TABLE 12

Manufacturers of RH Sensors and Readout Meters

Phys-Chem Research Corporation
36 West 20th Street
New York, New York 10011

Weathertronics, Inc
2777 Del Monte Street
West Sacramento, California 95491

American Instrument Company
8030 Georgia Avenue
Silver Spring, Maryland 20910

Delmhorst Instrument Company
117 Cedar Street
Boonton, New Jersey

Bacharach Instrument Company
2300 Leghorn Street
Mountain View, California 94043

General Eastern Instrument Corporation
36 Maple Street
Watertown, MA   02172

TABLE 13

Manufacturers of Various Detectors

13 a.   Manufacturers of FID's:

Beckman Instruments Inc.
Process Instruments Division
2500 Harbor Boulevard
Fullerton, California 92634

Century Systems Corporation
P.O. Box 133
Arkansas City, Kansas 67005

Mine Safety Appliances Company
600 Penn Center Boulevard
Pittsburgh, Pennsylvania 15235

Melay Labs, Inc.
6715 Electronic Drive
Springfield, Virginia 22151

Health Consultants, Inc.
100 Tascor Drive
Stranghton, MA 02071

Antek Instruments,Inc.
6005 N. Freeway
Houston, Texas 77076

Analytical Instruments Development Inc.
Route 41 & Newark Road
Avondale, Pennsylvania 19311

TABLE 13 (cont'd.)

Manufacturers of Various Detectors

13 b.   **Manufacturers of Infrared Analyzers:**

Foxboro Analytical
Box 5449
South Norwalk, Connecticut 06856

Sensors, Inc.
3908 Varsity Drive
Ann Arbor, Michigan 48104

Perkin-Elmer Corporation Industrial Division
Main Avenue
Norwalk, Connecticut 06856

Infrared Industries Inc.
P.O. Box 989
Santa Barbara, California 93102

CEA Instruments, Inc.
15 Charles Street
Westwood, New Jersey 07675

Bendix-Environmental and Process Division
1400 Taylor Avenue
Baltimore, Maryland 21204

TABLE 13 (cont'd.)

Manufacturers of Various Detectors

13 c.   ## Manufacturers of Photoionization Detectors

HNU Systems, Inc.
30 Ossipee Road
Newton, MA 02164

Aid Inc
Route 41 & Newark Road
Avondale, Pennsylvania 19311

13 d.   ## Manufacturers of Chemiluminescence Detectors

Thermo Electron
100 First Avenue
Waltham, MA 02154

Scott Environmental Systems
Division of ETC
County Line Industrial Park
Southampton, Pennsylvania 18966

Nutech Corporation
2806 Check Road
Durham, North Carolina 27704

Monitor Labs, Inc.
4202 Sorrento Valley Boulevard
San Diego, California 92121

Columbia Scientific Industries
Box 9908
Austin, Texas 78766

TABLE 14

Manufacturers of Mass Flow Meters

Hasting-Raydist
Hampton,
Virginia 23361

Sierra Instruments, Inc.
P.O. Box 909
Carmel Valley, California 93924

Kurz Instruments, Inc.
P.O. Box 844
Carmel Valley, California 93924

Tylan Corporation
19220 Normandie Avenue
Torrence, California 90502

TABLE 15

Manufacturers of Orifices

Millipore Corporation
Bedford,
Massachusetts 01730

Richard H. Bird and Company, Inc.
1 Spruce Street
Wotham, Massachusetts 02154

TABLE 16

Manufacturers of Manometers

Dwyer Instruments, Inc.
P.O. Box 373
Michigan City, Indiana 46360

The Meriam Instrument Company
10920 Madison Avenue
Cleveland, Ohio 44102

TABLE 17

Some Laboratory Supply Houses

Curtin Matheson Scientific, Inc.
4220 Jefferson Avenue
P.O. Box 1546
Houston, Texas 77001

Sargent-Welch Scientific Company
7300 North Linder Avenue
Skokie, Illinois 60076

Arthur H. Thomas Company
P.O. Box 779
Vine Street at 3rd
Philadelphia, Pennsylvania 19105

Fisher Scientific Company
711 Forbes Avenue
Pittsburg, Pennsylvania 15219

Ace Glass Incorporated
P.O. Box 688
1430 Northwest Boulevard
Vineland, New Jersey 08360

GCA/Precision Scientific
3737 West Courtland Street
Chicago, Illinois 60647

Markson Science, Inc.
522 Oak Street
Del Mar, California 92014

Cole-Parmer Instrument Company
7425 North Oak Park Avenue
Chicago, Illinois 60648

Bel-Art Products
Pequiannock,
New Jersey 07440

Lab Safety Supply Company
P.O. Box 1363
Janesville, Wisconsin 53545

TABLE 18

Sources of Constant Temperature Bath-Circulators

Forma Scientific, Inc.
P.O. Box 649
Marietta, Ohio 45750

Neslab Instruments
871 Islington Street
Portsmouth, New Hampshire 08801

Lab-Line Instruments, Inc.
Lab Line Plaza
Melrose Park, Illinois 60160

B. Barun Instruments
805 Grandview Drive
South San Francisco, California 94080

GCA Precision Scientific
3737 West Cortland Street
Chicago, Illinois 60647

Blue M Electric Company
138th & Chatham Streets
Blue Island, Illinois 60406

Fisher Scientific Company
711 Forbes Avenue
Pittsburgh, Pennsylvania 15219

TABLE 19

Some Contaminants Generated by Various Methods

Vapor Pressure	Permeation Tubes	Syringe Pump	Cylinder Dilution
Trichloroethylene	NO_2	Methylene Chloride	CO
Mercury	SO_2	Epichlorohydrin	CO_2
Methylene Chloride	H_2S	Acrolein	Methane
Toluene	NH_3	CS_2	NH_3
Acetone	Cl_2	Hexane	Vinyl Chloride
Hexane	Vinyl Chloride	MEK	Arsine
Styrene	Acrylonitrile		Nickel Carbonyl
Carbon Disulfide	HCN		Hydrogen Fluoride
MEK			Ethylene Oxide
TDI			N_2O
Benzene			Methyl Chloride
Epichlorohydrin			
Methyl Alcohol			
PCB's			
Diethylmercury			
Dimethylmercury			
2-Nitropropane			
Acrylonitrile			
DBCP			
Trichloronitromethane			
Dimethylethylamine			
Vinylidene Chloride			

FIGURES

STATIC GENERATION SYSTEM COMPONENTS

FIGURE 1

DILUTION AIR STREAM
PURIFIED AIR FROM GENERATOR

FLOW CONTROL AND
MEASUREMENT

MIXING CHAMBER

VENT

MANIFOLD OR
SAMPLING BALL

GAS CYLINDER

ROTAMETER

LIMITING ORIFICE

MASS FLOW METER

FINE METERING VALVE

CONTAMINANT STREAM
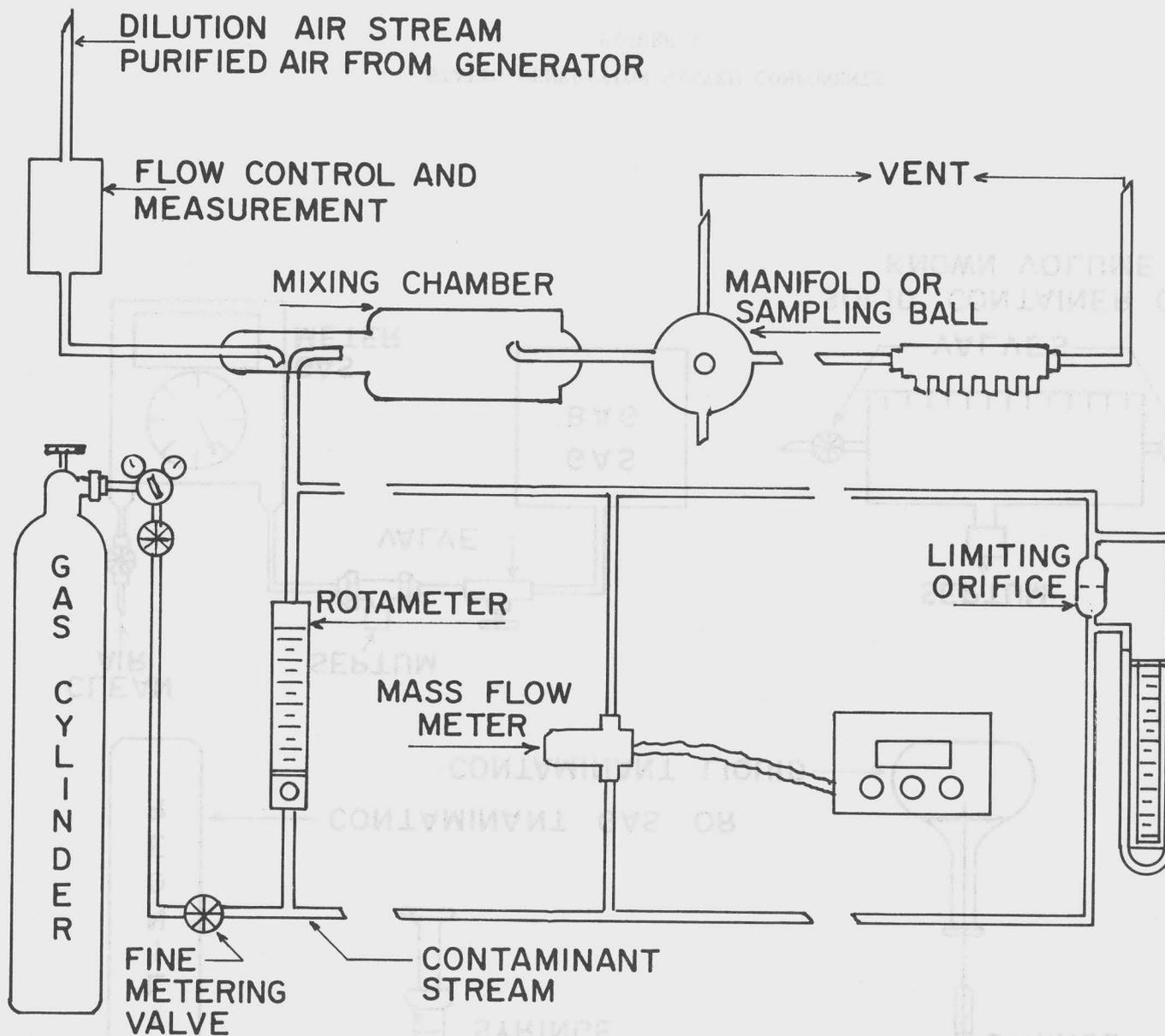
CYLINDER DILUTION SYSTEM

FIGURE 2

DILUTION AIR STREAM
PURIFIED AIR FROM
GENERATOR

CONTAMINANT STREAM

MIXING
CHAMBER

MOLECULAR
SEIVE

SAMPLING
BULB OR
MANIFOLD

PERMEATION
TUBES

NEEDLE
VALVE

CONDENSER

CONSTANT
TEMP. BATH

MASS
FLOWMETER

ROTAMETER
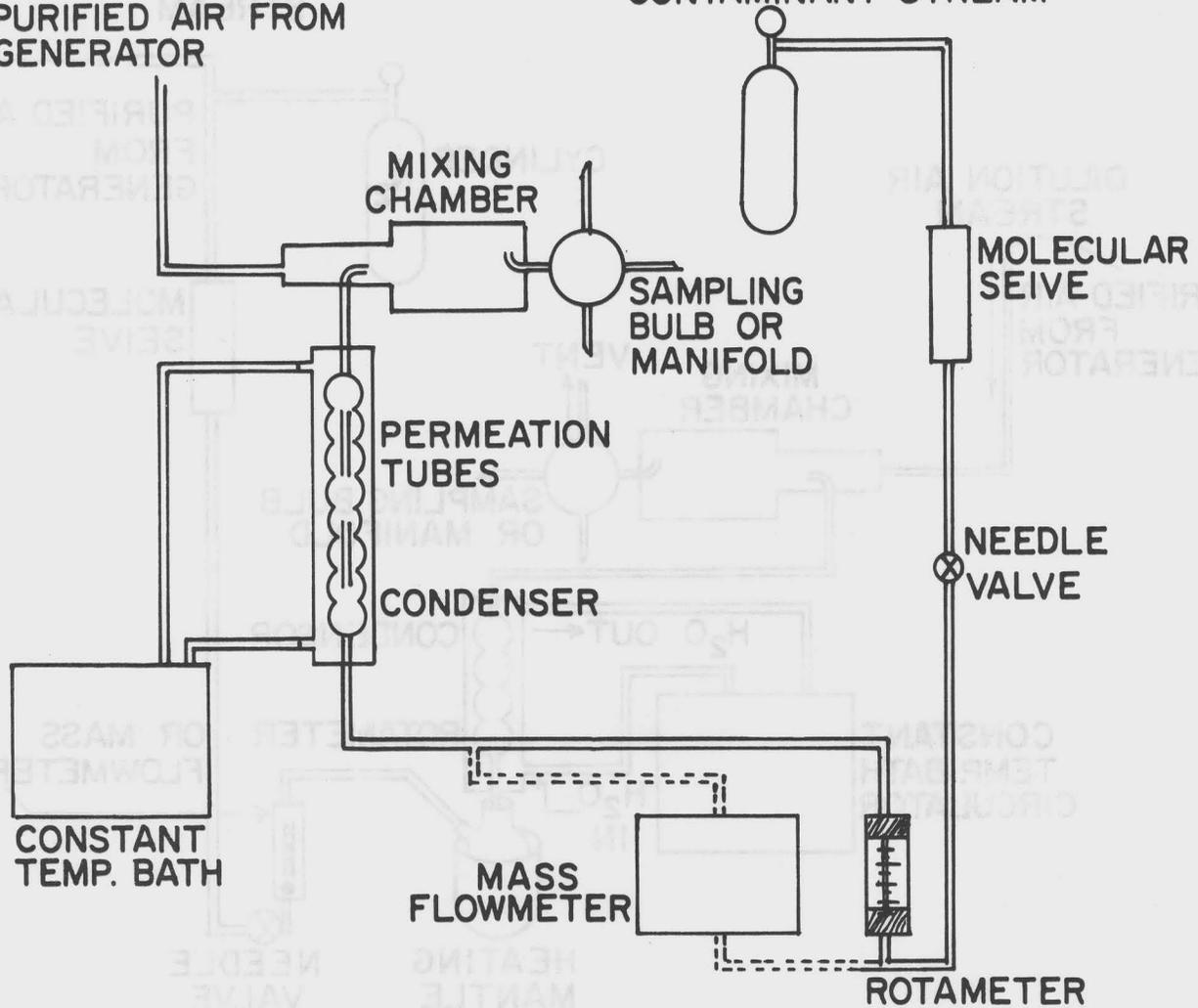
PERMEATION TUBE GENERATION SYSTEM
FIGURE 3
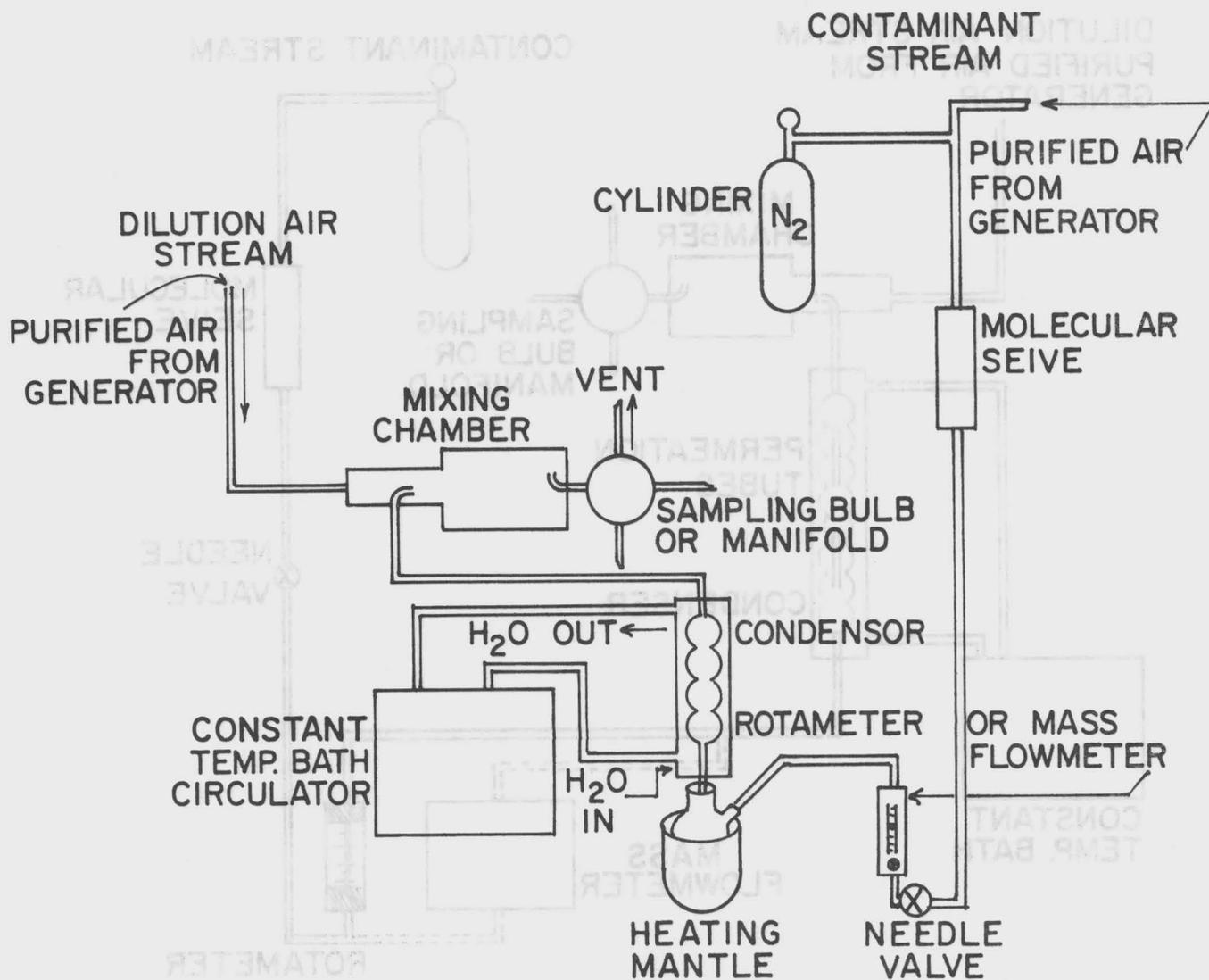
VAPOR PRESSURE GENERATION SYSTEM
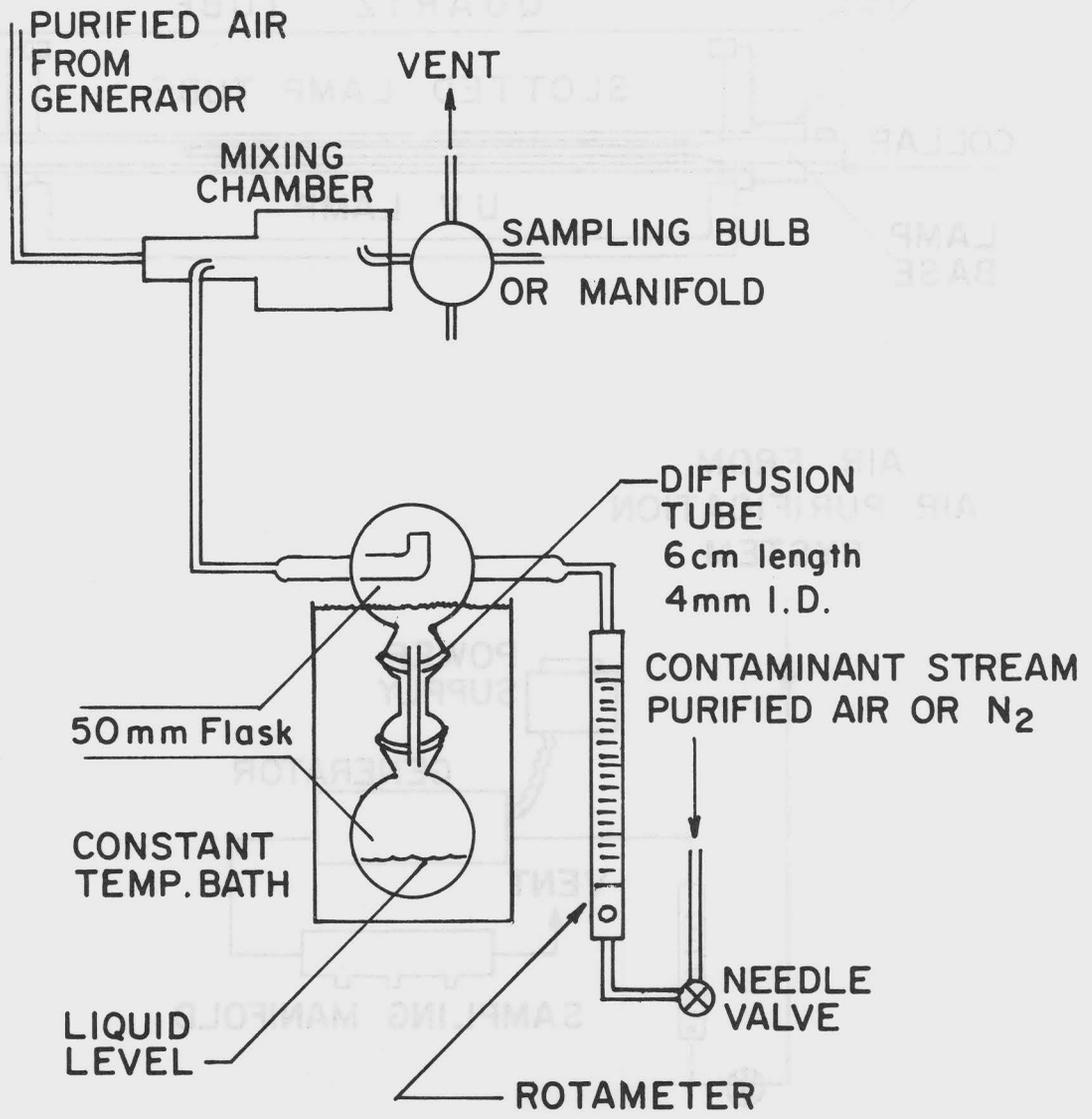FIGURE 4a
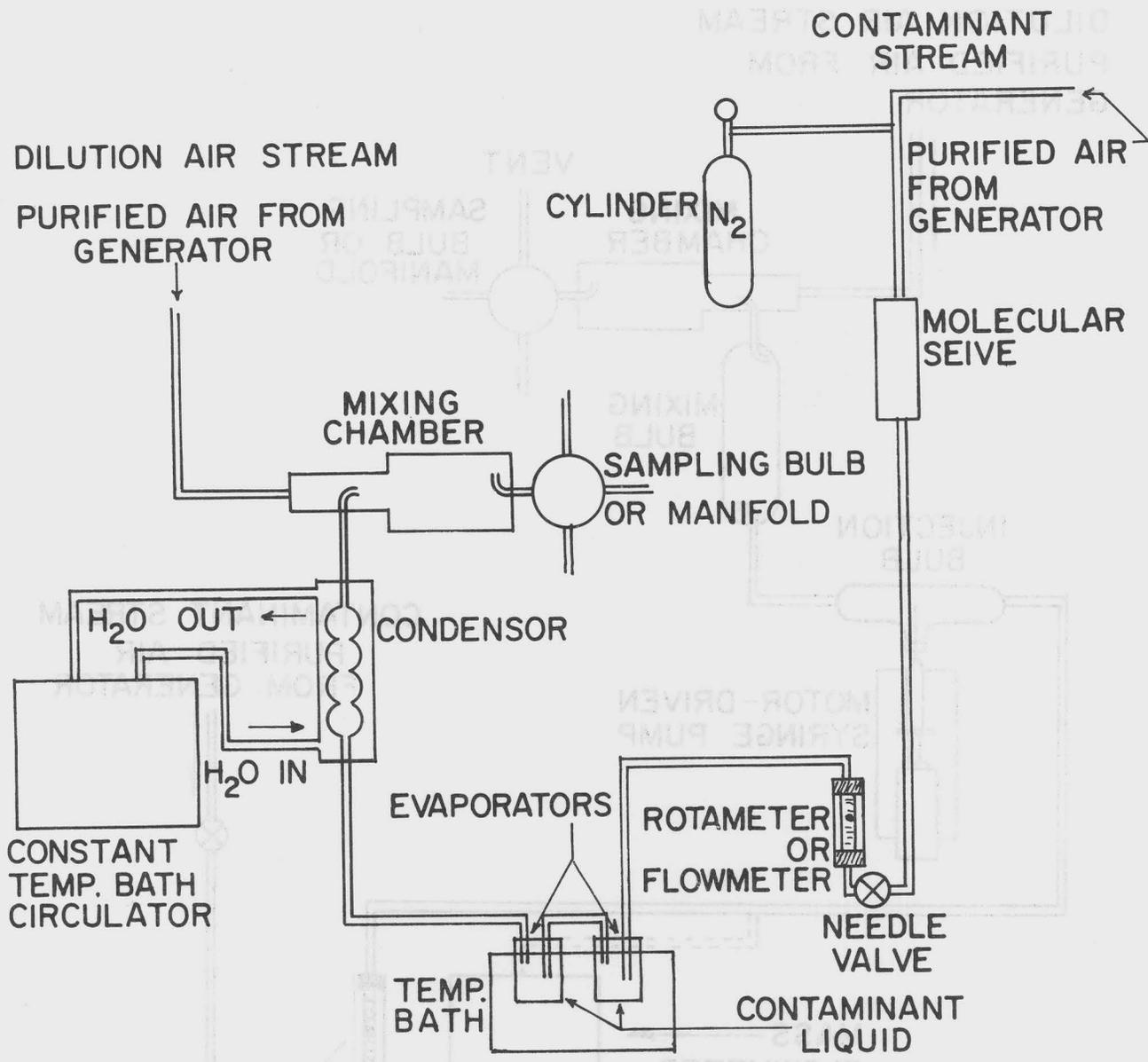
VAPOR PRESSURE GENERATION SYSTEM

FIGURE 4b
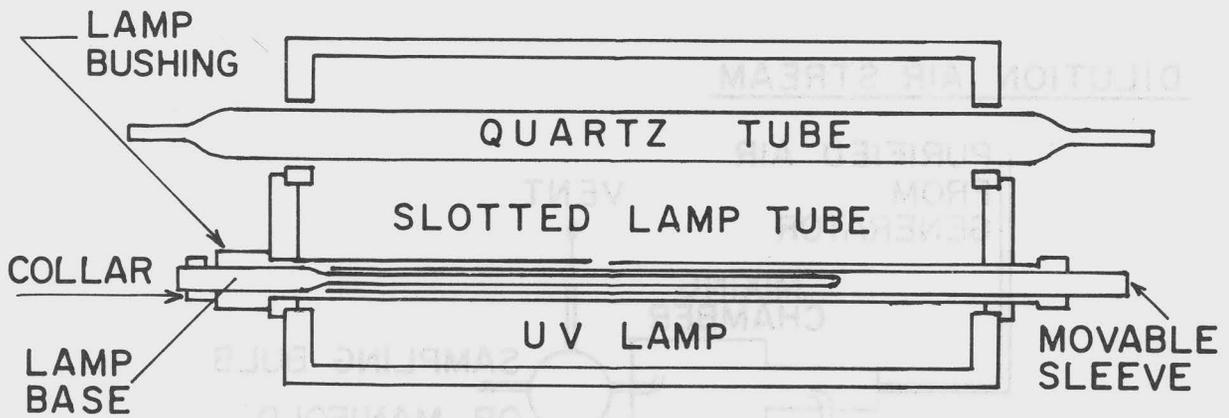
DILUTION AIR STREAM
PURIFIED AIR FROM
GENERATOR

VENT

MIXING
CHAMBER

SAMPLING
BULB OR
MANIFOLD

MIXING
BULB

INJECTION
BULB

CONTAMINANT STREAM
PURIFIED AIR
FROM GENERATOR

MOTOR-DRIVEN
SYRINGE PUMP

MASS
FLOWMETER

ROTAMETER
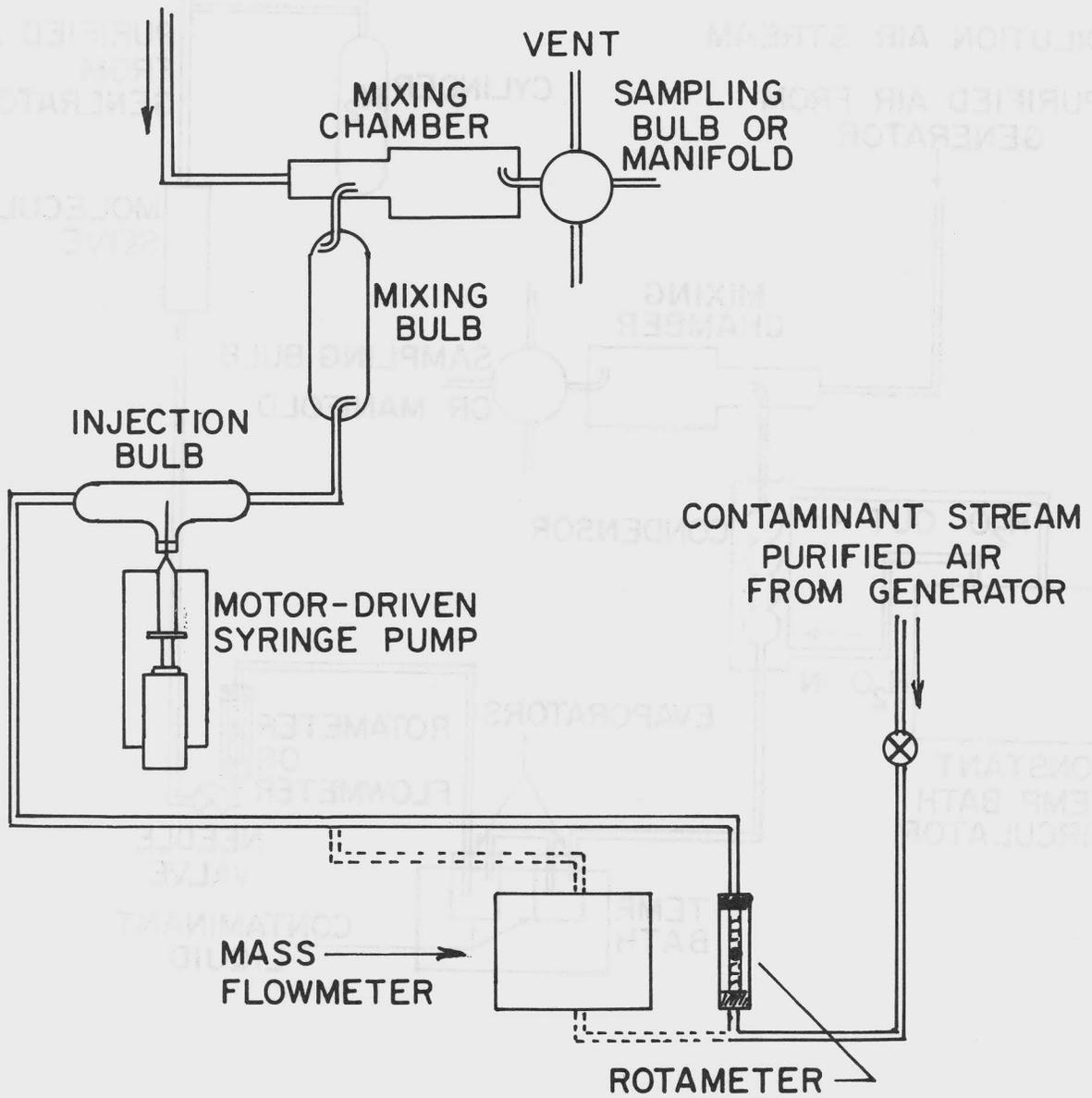
SYRINGE PUMP GENERATION SYSTEM

FIGURE 5

DILUTION AIR STREAM

PURIFIED AIR
FROM
GENERATOR

VENT

MIXING
CHAMBER

SAMPLING BULB
OR MANIFOLD

DIFFUSION
TUBE
6 cm length
4 mm I.D.

50 mm Flask

CONTAMINANT STREAM
PURIFIED AIR OR N_2

CONSTANT
TEMP. BATH

NEEDLE
VALVE

LIQUID
LEVEL

ROTAMETER

DIFFUSION TUBE GENERATION SYSTEM

FIGURE 6

LAMP
BUSHING

QUARTZ TUBE

SLOTTED LAMP TUBE

COLLAR

U V LAMP

LAMP
BASE

MOVABLE
SLEEVE

AIR FROM
AIR PURIFICATION
SYSTEM

POWER
SUPPLY

GENERATOR

VENT
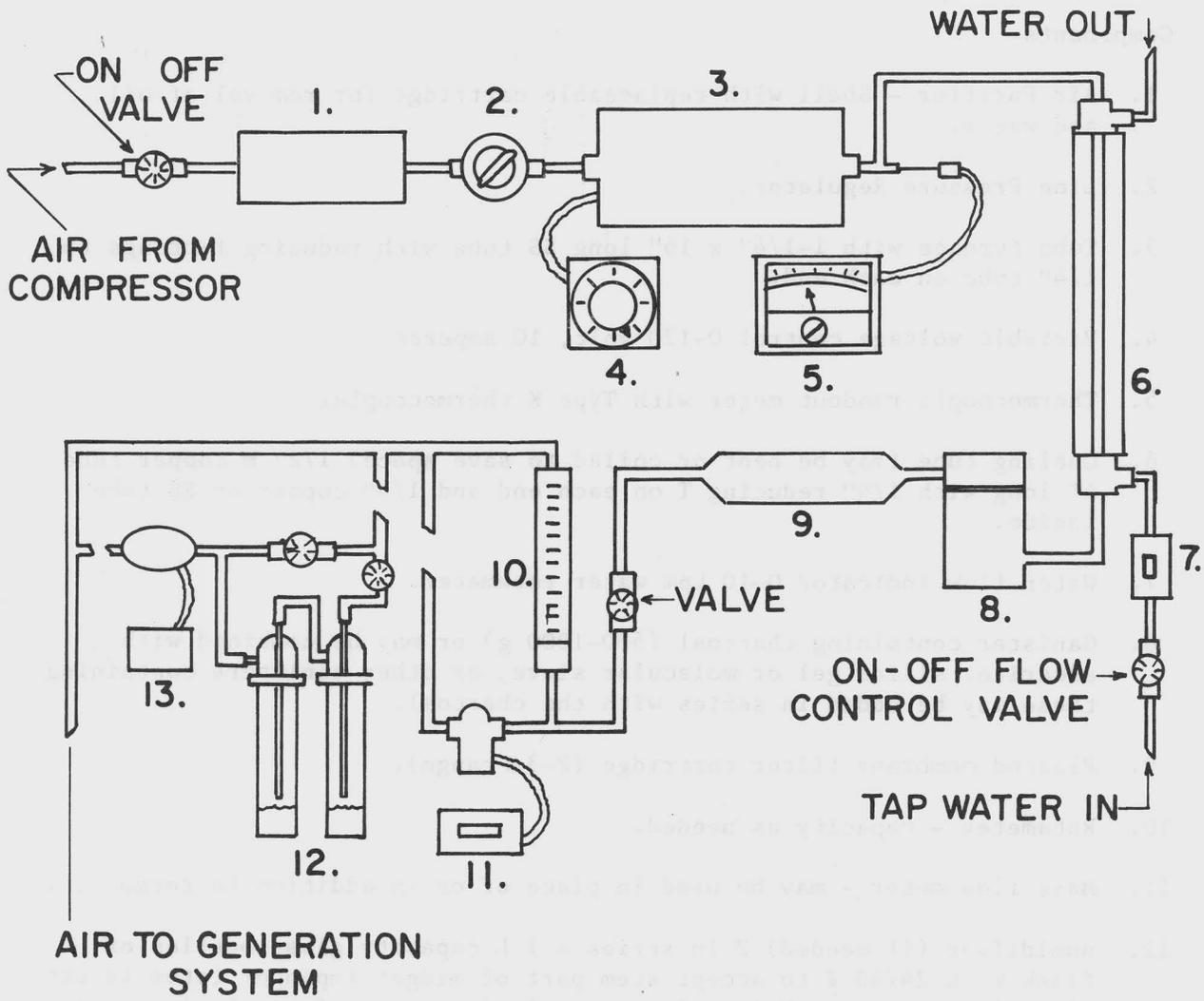
SAMPLING MANIFOLD
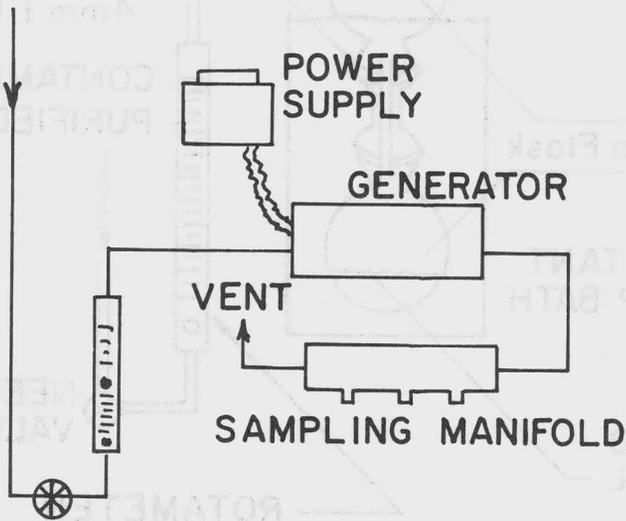
AIRFLOW MEASUREMENT
AND CONTROL

OZONE GENERATION SYSTEM
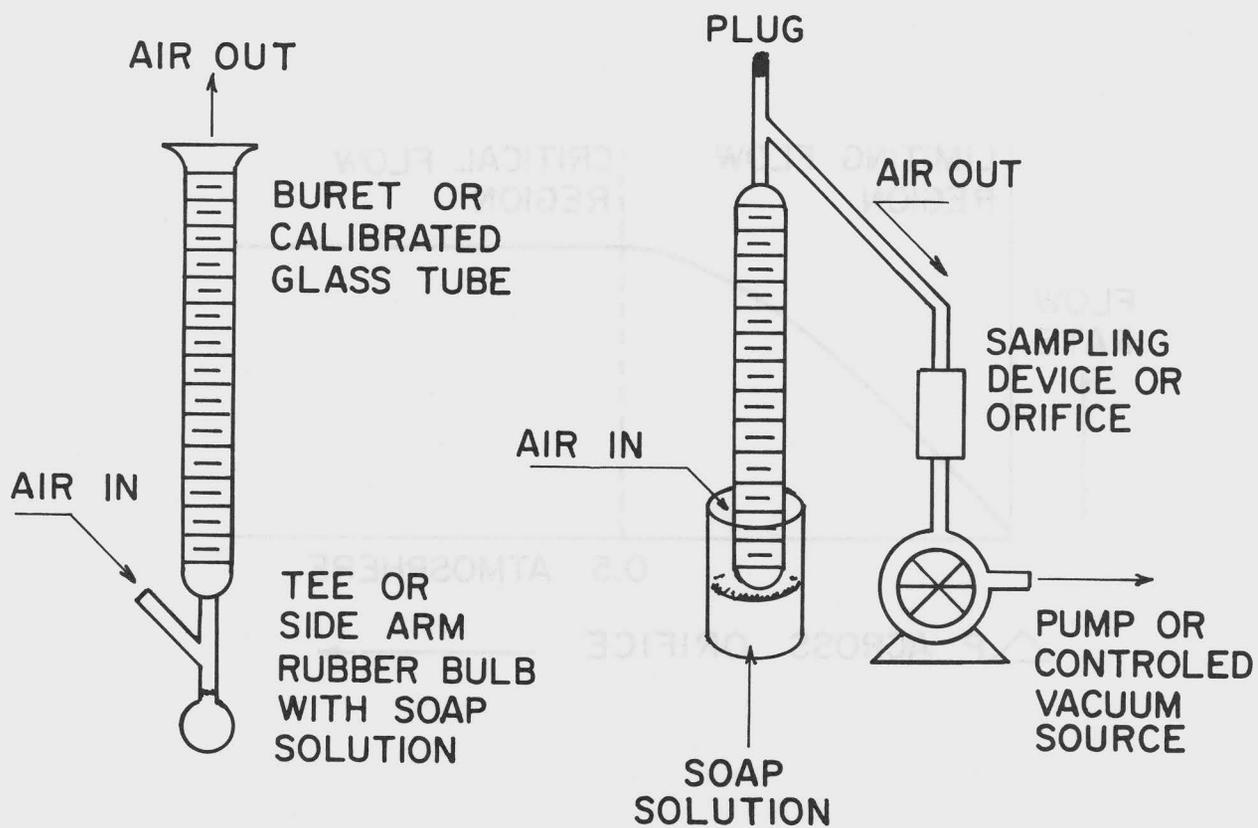
FIGURE 7

Figure 8—LEGENDS

Components

1. Air Purifier — Shell with replaceable cartridge for removal of oil and water.

2. Line Pressure Regulator.

3. Tube furnace with 1-1/4" x 16" long SS tube with reducing fittings to 1/4" tube on each end.

4. Variable voltage control 0-120 volt, 10 amperes.

5. Thermocouple readout meter with Type K thermocouple.

6. Cooling tube (may be bent or coiled to save space) 1/2" M copper tube 4' long with 1/4" reducing T on each end and 1/4" copper or SS tube inside.

7. Water flow indicator 0-10 Lpm water rotameter.

8. Canister containing charcoal (500-1000 g) or may be combined with ascarite, silica gel or molecular sieve, or other canisters containing these may be added in series with the charcoal.

9. Pleated membrane filter cartridge (2-3 μ range).

10. Rotameter — capacity as needed.

11. Mass flow meter — may be used in place of or in addition to rotameter.

12. Humidifier (if needed) 2 in series — 1 L capacity glass bottles of flask with 24/40 ₮ to accept stem part of midget impinger (stem is cut off before taper.) Valves for control of percent of total air passing over water. Additional flask may be added or flask may be heated if more humidity is needed.

13. Electronic Humidity Sensor-Readout Device.

ON OFF
VALVE

AIR FROM
COMPRESSOR

1.

2.

3.

WATER OUT

4.

5.

6.

10.

9.

VALVE

7.

8.

ON-OFF FLOW
CONTROL VALVE

TAP WATER IN

13.

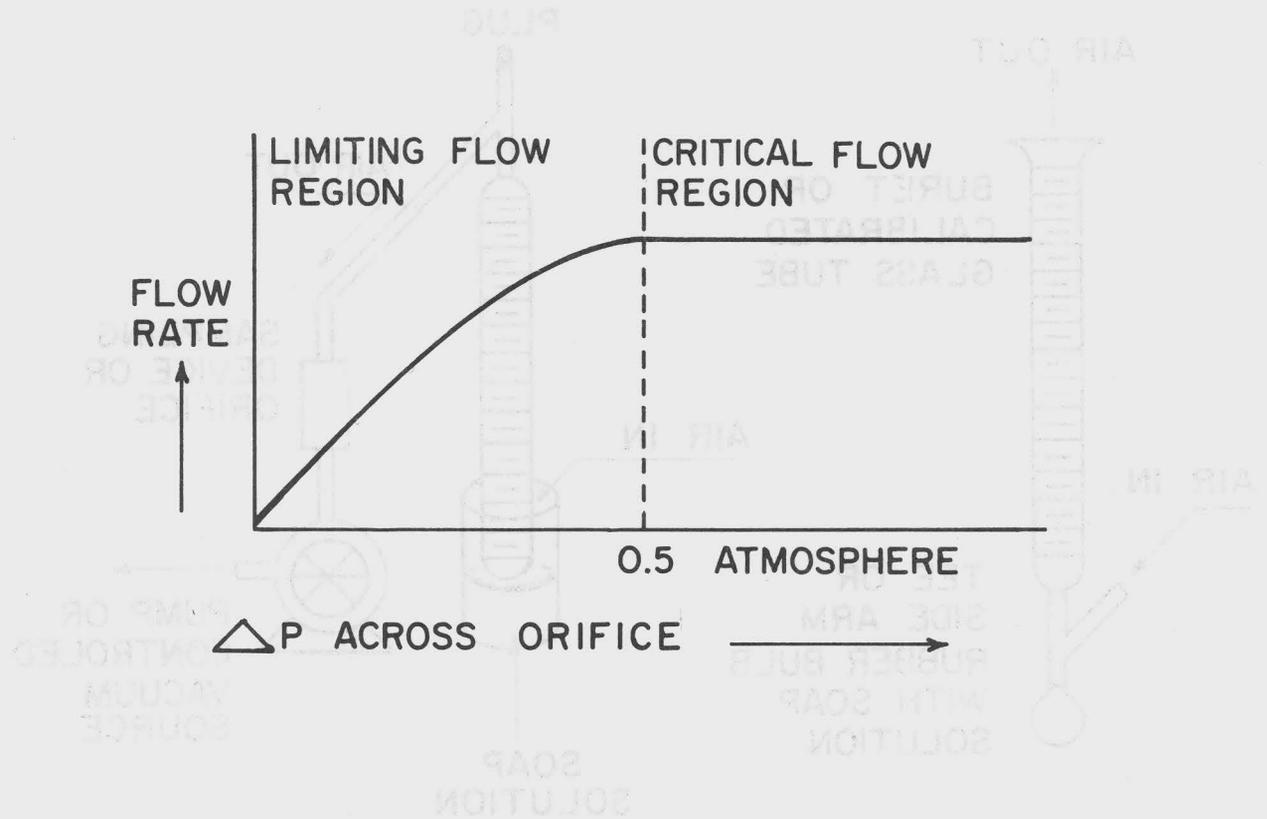12.

11.

AIR TO GENERATION
SYSTEM

AIR PURIFICATION & RH GENERATION

FIGURE 8

SOAP FILM FLOW METERS

FIGURE 9

ORIFICE FLOW DIAGRAM
FIGURE 10