CHAPTER 12

PREPARATION OF KNOWN CONCENTRATIONS OF AIR CONTAMINANTS

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INTRODUCTION

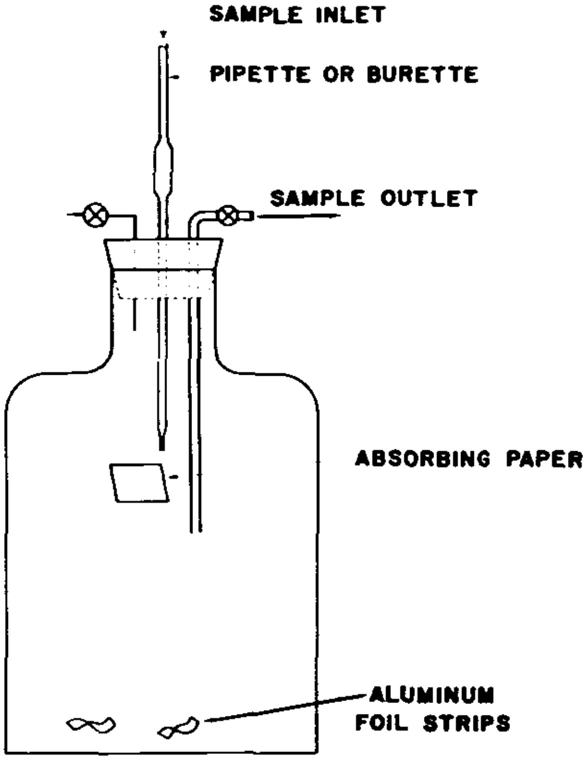
Known low concentrations of air contaminants are required for many purposes. There has been a technical explosion in recent years in the development of a great variety of monitoring instruments for measuring concentrations of air contaminants, based upon electronic means. These devices are invaluable; however, they are secondary measuring devices and must be calibrated. New chemical analytical procedures for air contaminants have been developed by extrapolating methods from the high concentrations at which they have been demonstrated to the low concentrations of interest. It is essential that these procedures be tested to demonstrate their validity. An extensive program of collaborative testing of methods at accurately known low concentrations is now beginning because of 1) the increase in regulatory activities and 2) the legal and economic consequence of measurements required to determine compliance. Another use for known concentrations is for toxicological and scientific investigations of the effects of these concentrations. Such work provides the basis for control standards. Thus known concentrations are essential for calibrating instruments, for collaborative testing of analytical methods and for scientific studies. When a highly precise system is employed, accurately known concentrations may be attained. With less accurate systems, the values are nominal. These may suffice for many purposes, or may be determined accurately by use of a standard or reference analytical procedure.

Two general types of systems are used for generating known concentrations. Preparation of a batch mixture has the advantage of simplicity and convenience in some cases. Alternatively, a flow-dilution system may be employed. This has the advantage of being capable of providing theoretically unlimited volumes at known low concentrations, which can be rapidly changed if desired, and of compactness. A flow-dilution system requires a metered source of diluent air, and a source for supplying known amounts of gases, vapors or aerosols; these flows are combined in a mixing device. The techniques will be described in detail below. Many articles have been published on this subject. Broad coverage is given in papers by Saltzman,[1] Cotabish et al.,[2] and Hersch.[3] A comprehensive book by Nelson is cited in the Preferred Reading section.

PREPARATION OF BATCH MIXTURES OF GASES AND VAPORS

Introduction

Known concentrations of gases and vapors were first prepared by introducing accurately measured quantities of the test compound into an appropriate chamber containing clean air. Various modified systems have been developed for certain special purposes. These methods generally require relatively simple equipment and procedures. However, a serious disadvantage is the fact that only limited quantities of the mixture can be supplied. In certain cases erroneously low concentrations result from appreciable adsorption losses of the test substance on the walls of the vessel. Losses in excess of 50% are common.[4-6] When air dilutions of solvents or other combustible materials are prepared, it should be borne in mind that there is a serious explosive hazard un-



Amer. Ind. Hyg. Assoc. J. 22:392, 1966.

Figure 12-1. 5 Gallon Mixing Bottle

less care is taken to keep the concentration outside of the explosive limits. These methods are convenient for many substances which are not too reactive. They may be used to prepare nominal concentrations, to be verified by chemical analyses. They should not be used as primary standards without such verification or prior experience.

Bottles

Figure 12-1 illustrates a simple technique for preparation of vapor mixtures utilizing a 5-gallon glass bottle. A quantity of volatile liquid is pipetted into the bottle onto a piece of paper to assist in its evaporation. The bottle may then be tumbled with aluminum foil inside to facilitate air and vapor mixing. The mixture is withdrawn through a glass tube from the bottom of the bottle rather than from the top to avoid leakage and losses occurring around the stopper. As the mixture is withdrawn, air enters the top of the bottle to relieve the vacuum. A sealed chamber may be used in a similar manner, with mixing provided by an electric fan. (Danger! Sparks from brushes may explode some mixtures!)

It can be seen that the disadvantage of this technique is that the concentration decreases during the withdrawal process. Assuming the worst possible case of complete turbulent mixing in the bottle or chamber, the change in concentration is given by equation 1.

$$C/C_0 = e^{-W/V} \qquad (1)$$

Where C = final concentration in bottle or chamber

C_0 = initial concentration

W = volume withdrawn, liters

V = original volume of mixture, liters

Some calculated values are shown in Table 12-1.

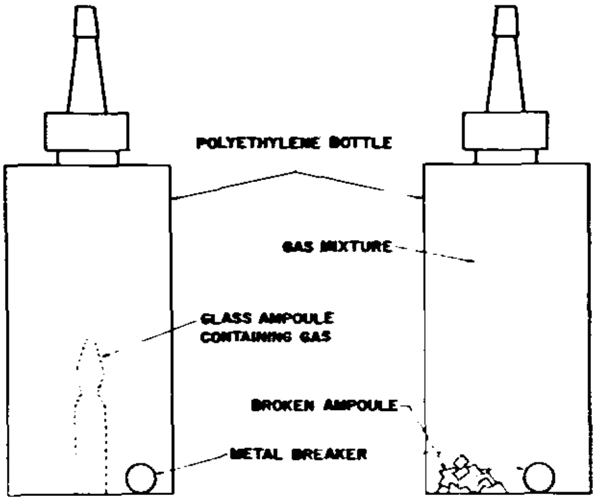
TABLE 12-1

Decrease in Concentration vs. Fractional Volume Withdrawn

W/V	0.05	0.10	0.25	0.50
C/C_0	0.962	0.905	0.779	0.606

This table shows the maximum depletion errors produced by withdrawal of the mixture. Smaller errors result if the incoming air does not mix completely with the existing mixture. Up to 5% can be withdrawn without serious loss. These errors are avoided by use of plastic bags or pressure cylinders, as described below.

Figure 12-2 indicates a simple commercial assembly for calibrating explosive-gas meters. A sealed glass ampule containing a hydrocarbon, such as methane, is placed inside a polyethylene bottle and broken by shaking against a steel ball. The mixture is then carefully squeezed into the instrument to be calibrated, taking care not to suck back air. Another similar instrument manufactured by Mine Safety Appliances Co. is comprised of a cartridge of isobutane which is used to fill a small syringe. This is injected into a larger syringe which is then filled with air. The latter syringe serves as a gas holder for the mixture. These devices are relatively simple, convenient and sufficiently accurate for this purpose.



Amer. Ind. Hyg. Assoc. J. 22:392, 1966.

Figure 12-2. J-W Gas Indicator Test Kit

Plastic Bags

A variety of plastic bags have been found to be very useful for preparing known mixtures in the laboratory. Long term stability is generally good only with relatively inert vapors such as of halogenated solvents and hydrocarbons. Among the materials used have been Mylar, Scotchpak, Saran and polyvinyl chloride. Bags are fabricated from sheets by thermal sealing. Mylar bags are popular because of their strength and inertness. This material requires a special thermal plastic adhesive tape (Schjeldahl). Tedlar, Teflon and Kel-F are considerably more expensive materials, which also require expensive sealing equipment capable of providing regulated pressures and high temperatures. They are preferred for use in photochemical studies involving ultraviolet irradiation. Surprisingly, for most applications the less expensive materials give superior performance. Volatile contaminants may be baked out of the sheets by keeping them in an oven for a few days. A valve of the type used for tires, or a rigid plastic tube may be sealed to a corner to serve as the inlet. The inlet tube to the bag may be closed with a rubber stopper or serum cap, a cork or a valve according to the material being handled. Bags are available commercially. The 3′ x 3′ or 2′ x 4′ size contains over 100 liters.

The major advantage of using flexible bags is that no dilution occurs as the sample is withdrawn. These bags also are very handy for sampling purposes since the empty bags are transportable. Bags should be tested frequently for pinhole leaks. This may be done by filling them with clean air and sealing them. If no detectable flattening occurs within 24 hours, the leakage is negligible.

A simple arrangement may be used for preparing a known mixture in a plastic bag. The bag is alternately partly filled with clean air and then completely evacuated several times to flush it out. Then clean air is metered into it through a wet or dry test meter. The test substance is added to this stream at a tee just above the entrance to the bag. If it is a volatile liquid, it can be injected with an accurate syringe through a septum. Sufficient air must subsequently be passed through the tee to completely transfer the injected material. When the desired volume has been introduced, the bag is disconnected and plugged or capped. Its contents may be mixed by gently kneading the bag with the hands.

Adsorption and reaction on the walls is no great problem for relatively high concentrations of inert materials.[6] However, low concentrations of reactive materials such as sulfur dioxide, nitrogen dioxide and ozone are partly lost, even after prior conditioning of the bags.[4,5,7,8] Larger sizes are preferable to minimize the surface-to-volume ratio. Losses of 5 or 10% frequently occur during the first hour, after which the losses are a few percent a day. Conditioning of the bags with similar mixtures is essential to reduce these losses. The similar or identical mixture is stored for at least 24 hours in the bag, and then evacuated just before use.

A recent compilation by Schuette[9] lists the commercial sources of these plastic sheets and needed accessories. A tabulation is presented of uses described in 12 papers, listing the plastic material, the gas or vapor stored, their concentrations and comments. Another recent study[10] focussed upon industrial hygiene applications. Good stability in Saran bags was found for mixtures containing benzene, dichloromethane and methyl alcohol; and for Scotchpak bags containing benzene, dichloromethane and methyl isobutyl ketone. Percentage losses were greater for lower concentrations (i.e., 50 ppm). Losses greater than 20% were observed in the first 24 hours for Saran bags containing methyl isobutyl ketone vapors, and for Scotchpak bags containing methyl alcohol vapors; however, concentrations stabilized after 2 to 3 days. These results are typical of those obtained by the other investigators previously cited.

It is difficult to draw generalized conclusions from these reports, other than the need for caution in applying plastic bags for low concentrations. Losses should be determined for each material in each type of bag. Even the past history of the bag must be considered. For laboratory applications properly conducted, known mixtures can be prepared very conveniently in plastic bags.

Pressure Cylinders

Preparation of certain gas mixtures can be done conveniently in steel cylinders.[2] This is very useful for mixtures such as hydrocarbons in air or carbon monoxide in air, which can be stored for years without losses. With other substances, there are losses due to factors such as polymerization, adsorption, or reaction with the walls. In some cases, as the pressure decreases in the cylinder, material desorbs from the walls and yields a higher final concentration in the cylinder than was initially present. Concentrations should be low enough to avoid condensation of any component at the high pressure in the cylinder, even at the lowest temperature expected during its use. Care must be taken to use clean regulators, of appropriate materials, which will not adsorb or react with the contents of the cylinder. A serious safety hazard exists in preparation of compressed gas mixtures. As mentioned previously, there is a possibility of explosion of combustible substances. This may occur because of the heat of compression during a too rapid filling process. Excessive heat also may cause errors in the gas composition. Certain substances with a high positive heat of formation, such as acetylene, can detonate even in the absence of oxygen. Also, explosive copper acetylid can be produced if this metal is used in the manifolds and connections. Proper equipment, including armor-plate shielding, and experience are required for safe preparation. Because these and accurate pressure gauges are not ordinarily available, it is recommended that the mixtures be purchased from the compressed gas vendors who have professional staff, experience and equipment for such work. These vendors can prepare mixtures either by using accurate pressure gauges to measure the proportions of the components or by actually weighing the cylinders as each component is added. They also can provide an analysis at a reasonable extra charge; however, these figures are not always reliable.

Calculations

The calculations for preparation of batch mixtures are based upon the close adherence to the Perfect Gas Law that is usual at low partial pressures. Calculations for dilute gas concentrations are based upon the simple ratio of the volume of test gas to the volume of mixture, as shown in equation 2.

$$\text{P.P.M.} = 10^6\, v/V \qquad (2)$$

Where P.P.M. = parts per million by volume
v = volume of test gas in mixture, liters
V = volume of mixture, liters

In the case of volatile liquids the calculation is based upon the ratio of moles of liquid to moles of gas mixture, equation 3. The moles of liquid are determined by dividing the weight injected by the molecular weight of the liquid. The moles of gas mixture are calculated by dividing the total volume of mixture by the molecular volume calculated from equation 4 for the temperature and pressure of the mixture.

$$\text{P.P.M.} = \frac{10^6\, w/\text{M.W.}}{V/\overline{V}} \qquad (3)$$

$$\overline{V} = 24.47\left(\frac{760}{P}\right)\left(\frac{t+273.2}{298.2}\right) \qquad (4)$$

where w = weight of volatile liquid introduced, grams
M.W. = gram molecular weight of liquid
$\overline{V}$ = gram molecular volume of mixture under ambient conditions, liters
P = ambient pressure, Torr
t = ambient temperature, °C

These calculations are illustrated by the following:

Example 1. A volume of 5 ml of pure carbon monoxide is added to a plastic bag into which 105 liters of air are metered. What is the concentration (ppm by vol.) of the carbon monoxide?

Answer:

$$\text{P.P.M.} = 10^6 \times 0.005/105 = 47.6$$

Example 2. A dish containing 12.7 g of carbon tetrachloride is placed in a sealed cubical chamber with inside dimensions of 2.1 meters for each edge. The final temperature is 22.5° C, and the barometer reading is 755 mm. Hg. What concentration (ppm by vol.) is achieved?

Answer:

$$\text{M.W. of } CCl_4 = 12.01 + 4 \times 35.457 = 153.84$$

$$\overline{V} = 24.47 \times \left(\frac{760}{755}\right) \times \left(\frac{295.7}{298.2}\right) = 24.43$$

$$\text{P.P.M.} = \frac{16^6 \times 12.7/153.84}{1000 \times (2.1)^3/24.43} = 217.7$$

FLOW-DILUTION SYSTEMS

Introduction

Flow-dilution systems offer the advantage of being very compact. Since it is possible to operate them continuously, there is no theoretical limit to the volumes of gas mixture that can be provided. In a properly designed system, concentrations can be changed very rapidly. Because of the relatively small gas volume of this system, the explosive hazard is less than that of batch systems. Any losses by adsorption on surfaces occur only in the initial minutes of operation. After a brief period, the surfaces are fully saturated and no further losses occur. Because of these advantages, flow-dilution systems are popular for accurate work with most substances.

Gas-Metering Devices

A variety of devices can be used to monitor the flows in a flow-dilution system. The accuracy of final concentration is, of course, dependent upon the accuracy of the measurements of the component flows. Rotometers are commonly used. Orifice meters and critical orifices are also frequently employed. The calibration equations and techniques are given in detail in Chapter 11. Because rotometers are very commonly used, a few points of importance to this application will be discussed.

The pulsating flows provided by the diaphragm pumps utilized in many systems may result in serious errors in most meter readings. Rotometer readings may be high by a flow factor of as much as 2, depending upon the wave form of the pulsating flow. It is therefore essential for accurate measurements to damp out such pulsations by assembling a train comprised of the pump, a surge chamber and a resistance, such as a partially closed valve. The error can be determined by running the pulsating flow through the rotometer and into a wet-test meter, and comparing the two measurements. The latter should be taken as correct. The reason for this error is that although the flowrate passing through the rotometer is proportional to the first power of the gas velocity, the lifting force on the ball is proportional to the velocity raised to a power of between 1 and 2. For completely turbulent flows, which are common, the exponent is 2; in this case if the velocity fluctuates in a sine wave the ball position will correspond to the root mean square value, which is 1.414 times the correct mean value. If the wave form is spiked, even greater deviations occur.

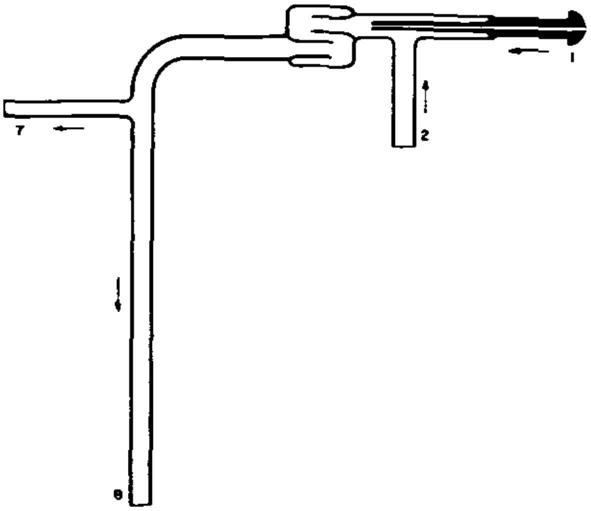
There are two types of corrections of flow meter calibrations for ambient pressure and temperature. The first is the correction to the actual flow because of the fact that the measured value is dependent upon the density and in some cases the viscosity of the gas flow, both of which are affected by ambient pressure and temperature. Application of the appropriate correction factor to the value from a calibration graph made under standard pressure and temperature conditions then will give the correct actual gas flowrate under ambient conditions. A second correction may be applied to convert the actual gas flowrate to that under standard conditions. This latter correction is made on the basis of the perfect gas equation. It should be kept clearly in mind that the first calibration correction is dependent upon the specific device being employed. The two bases, ambient or standard conditions, should not be confused, and the proper one must be employed for the application.

Construction and Performance of Mixing Systems

A flow-dilution system is comprised of a metered test substance source, a metered clean-air source and a mixer to dilute the test substance to the low concentration required. The total flow of mixture must be equal to or greater than the flow needed. It is highly desirable to use only glass or Teflon parts for constructing the system. Some studies have been made with metal and plastic tubing which have shown that these must be conditioned with the dilute mixtures for periods of hours or days before they cease absorbing the test substances.[4,5,11]

Two other factors must be kept in mind in the construction of a mixing system. The pressure drops must be very small and the system should preferably be operated at very close to atmospheric pressure. Otherwise, any changes in one part of the system will require troublesome readjustment of the flows of other components. The interactions may require several time-consuming reiterative adjustments. The second factor to consider is that the dead volume of the system must be minimized to achieve a rapid response time. For example, assume that we are metering a flow of 0.1 ml/min. into a diluent air stream, and that the dead volume of the system to the dilution point is 1 ml. To accomplish one volume change will require 10 minutes. In order to be certain that this dead volume is completely flushed out, five volume changes are needed, corresponding to a time lag of 50 minutes before the full concentration of test gas reaches the dilution point.

Figure 12-3 illustrates a convenient all-glass system for making gas dilutions. The test gas is connected at the extreme right through a ball joint



Anal. Chem. 33:1100, 1961.

Figure 12-3. All Glass System

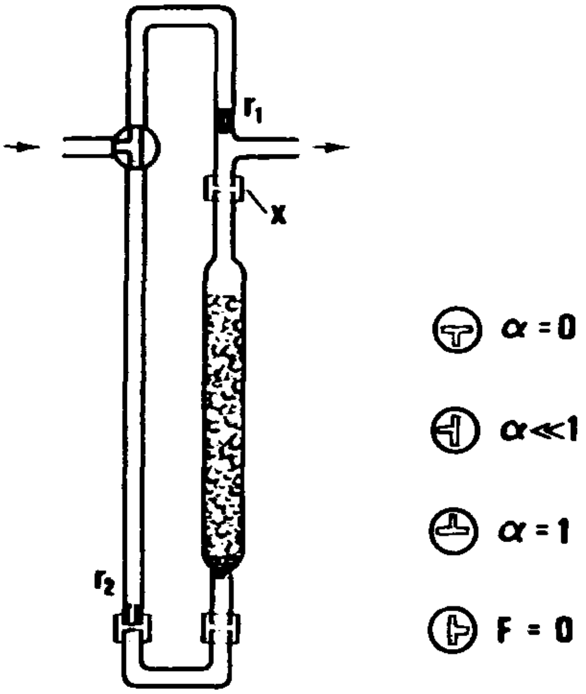
and capillary tube. The dilution air is metered into the side arm. A trap-like mixing device insures complete mixing with very little pressure drop. The desired flow can be taken from the side arm, and the excess vented through the waste tube which may be connected to a Tygon tube long enough to prevent entrance of air into the flow system. If desired, this vent tube can be run to a hood or adjacent window. By clamping down on the vent tube any desired pressure can be obtained in the delivery system.

The dilution air must be purified according to the needs of the work. Air can be passed over a bed of carbon, silica gel, or ascarite, or bubbled through a scrubbing mixture of chromic acid in concentrated sulfuric acid if necessary. Another convenient method of purification is to pass the air flow through a universal gas mask canister. The purification system must be designed according to the specific needs of the work.

SOURCE DEVICES FOR GASES AND VAPORS

Introduction

A variety of source devices are described below for providing high concentrations of gases and vapors which can be diluted with pure air to the level desired. Each possesses specific advantages and disadvantages. Selection of a device depends upon the needs of application and the equipment available to the user. Figure 12-4 shows a self-dilution device that can be generally applied to reduce the concentration provided by the source when necessary for work at very low concentrations. The flow of gas or vapor passes through two branches in proportions determined by restricters R_1 and R_2. An appropriate absorbent such as carbon, soda lime, etc. in the latter branch completely removes the gas or vapor from the stream. Thus the combined output of the two branches provides the same flow at a fractional concentration of the input depending upon the relative values of the two flow restricters. Furthermore, rotation of the three-way stopcock also provides either the full concentration or zero concentration, or completely cuts off the flow.



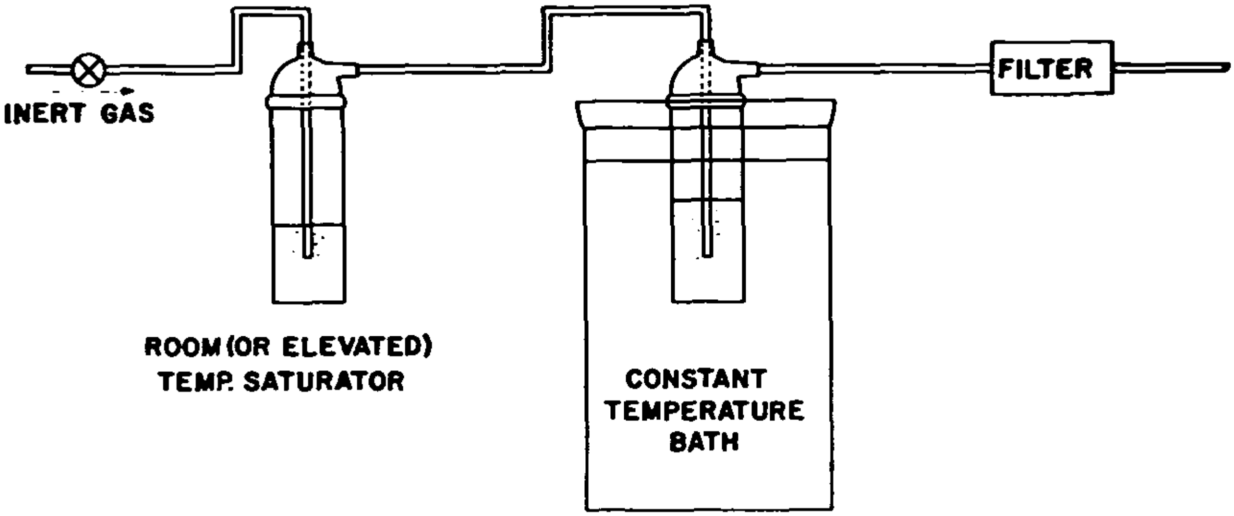
J. Air Pollution Control Assoc. 19:164, 1969.

Figure 12-4. Self-Dilution Device

Vapor Pressure Method

Figure 12-5 illustrates the vapor pressure method for providing a known concentration of a volatile liquid. A flow of inert gas or purified air is bubbled through a container of the pure liquid. Liquid mixtures are less desirable because the more volatile components evaporate first and the vapor concentrations change as the evaporation proceeds. In the common bubbler only 50 to 90% of the saturation vapor pressure is usually obtained. Equilibrium concentrations therefore are obtained by operating the bubbler at ambient or elevated temperature and passing the vapor mixture through an accurately controlled constant temperature bath which cools it down. The excess vapor is condensed, and the final concentration is very close to equilibrium vapor pressure at the cooling bath temperature. A filter must be included to insure that a liquid fog or mist does not escape. It is desirable to operate the constant temperature bath below ambient temperature so that liquid does not condense in the cool portions of system downstream. The application of this method to carbon tetrachloride has been described recently.[12]

Another version of this arrangement is shown in Figure 12-6. This utilizes a wick feed from a small bottle containing the additive as a source of



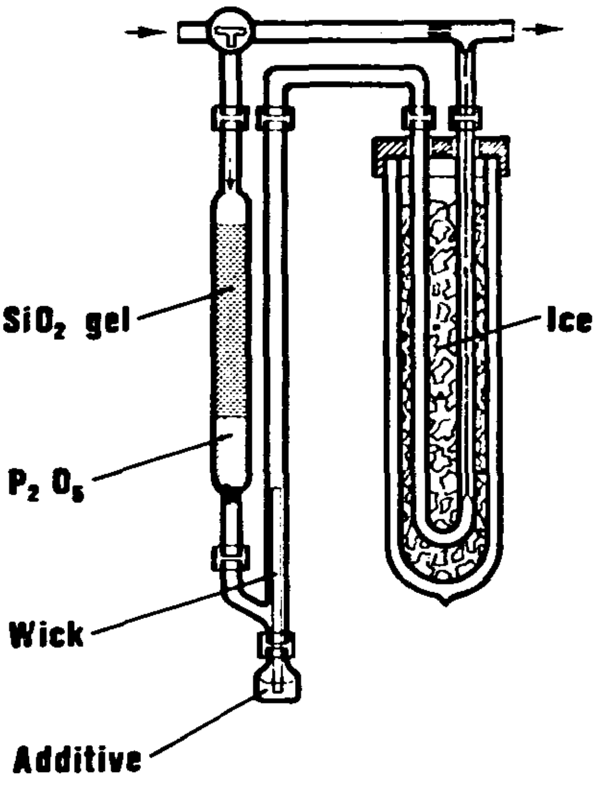
Amer. Ind. Hyg. Assoc. J. 22:392, 1966.

Figure 12-5. Vapor Saturator

the vapor, and an ice bath for the constant temperature.

Motor Driven Syringes

Figure 12-7 illustrates a system using a 50 or 100-ml glass hypodermic syringe which is driven by a motor drive at uniform rates that can be controlled to empty it in periods varying from a few minutes to an hour. A gas cylinder containing the pure component or mixture is connected at the right side. The bubbler is a safety device to protect the glass apparatus from excessive pressures if the tank needle valve is opened too wide. The tank valve is cautiously opened and a slow stream of gas vented from the bubbler. The syringe is manually filled and emptied several times to flush it with the gas. This is done by turning the three-way stopcock so that on the intake stroke the syringe is connected to the cylinder and on the discharge stroke to the delivery end. After flushing, the syringe is filled from the cylinder and the motor drive is set to discharge it over the desired period of time. This motor drive should include a limit switch to shut off the motor before it breaks the syringe, and a revolution counter for measuring the displacement. From the known gear ratio, the screw pitch and a measurement of the plunger diameter with a micrometer, the rate of feed can be calculated with an accuracy and reproducibility of parts per thousand.



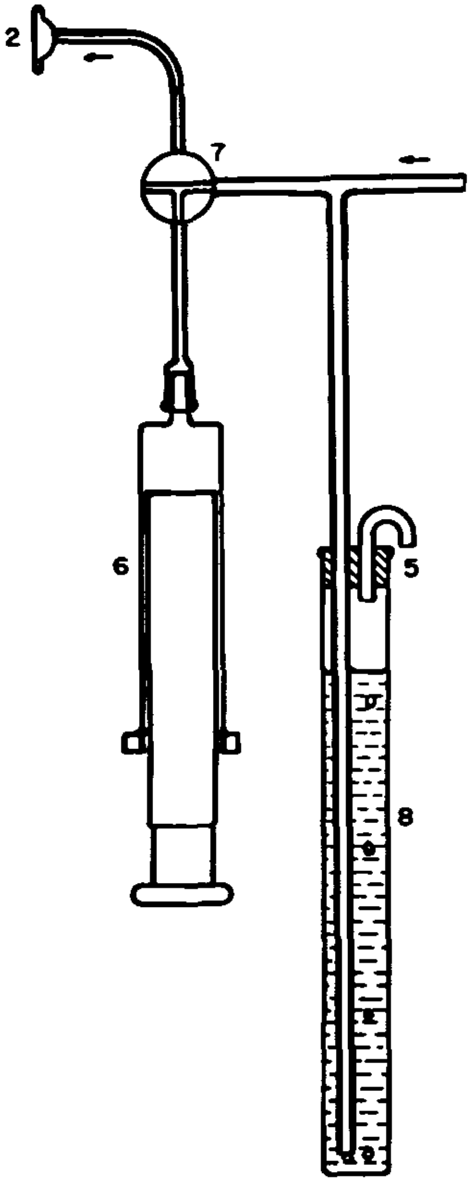
J. Air Pollution Control Assoc. 19:164, 1969.

Figure 12-6. Vapor Saturator

At low delivery rates the back diffusion of air into the syringe from the delivery tip may cause an error. Thus, if the syringe is set to empty over a one-hour period, towards the end as much as half of the gas mixture contents could be air that has diffused in backwards. This error is easily minimized by inserting a loose glass wool plug in the delivery system and using capillary tubing for the delivered flow.

Diffusion Systems

Figure 12-8 illustrates a diffusion system that can provide constant concentrations of a volatile liquid. The liquid is contained in the bottom of a long thin tube and is kept at a constant known temperature. As the air flow is passed over the top, vapor diffuses up through the length of the



Anal. Chem. 33:1100, 1961.

Figure 12-7. Motor Driven Syringe

tube at a reproducible rate and mixes with the stream. The rate is determined by the vapor pressure of the liquid, the dimensions of the tube and the diffusion constants of the vapor and of air. If substantial amounts of a liquid are evaporated and the liquid level drops, the diffusion path length increases slightly. The quantity of liquid evaporated can be determined from volume markings on the tube or by weighing the tube at the beginning and end of the period of use. Experimental values have been tabulated and the limitations of this method described.(13)

Porous Plugs

Figure 12-9 illustrates a micrometering system[1,14] that both measures and controls small flows of gas in the range of 0.02 to 10 ml/min.

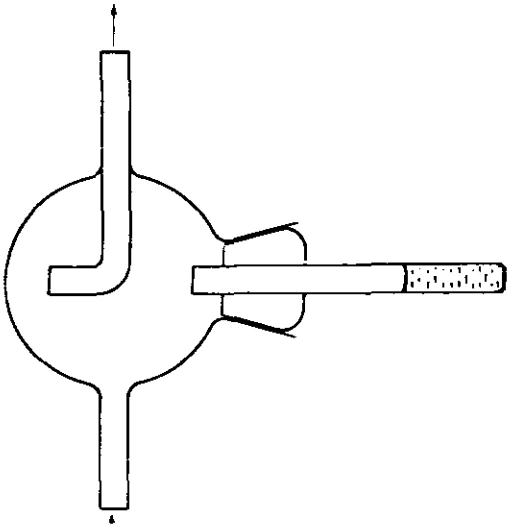


Figure 12-8. Diffusion System

This is based on the principle of diffusion of test gas through an asbestos plug under a controlled pressure difference. The input is connected to a

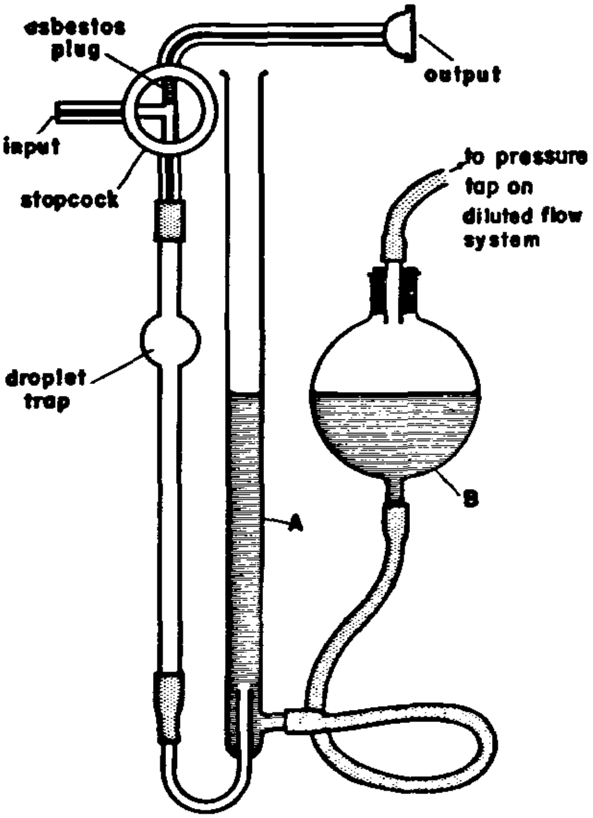


Figure 12-9. Micrometering System

cylinder containing pure gas or gas mixture. The asbestos plug is contained in one leg of the "T" bore of a 3-way stopcock as shown in the figure. The asbestos fiber is acid-washed, of the type used in the laboratory for Gooch crucibles. The degree of tamping is determined by trial and error to provide the desired flow range. The cylinder needle valve is opened cautiously to provide a few bubbles per minute from the waste outlet in the lower portion of the figure. The height of water or oil above the waste outlet determines the fixed pressure on the lower face of the asbestos plug, which produces a fixed rate of diffusion of the gas through the plug to the capillary delivery tip. The meter is calibrated by connecting the delivery end to a graduated 1-ml pipette with the tip cut off, containing a drop of water. The motion of the drop past the markings is timed with a stop watch. This is repeated for different heights of liquid obtained by adjustment of the levelling bulb. The calibration plot of flowrates in ml/min. against the heights of liquid over the waste outlet in cm. is usually a straight line passing through the origin. The gas cylinder should never be disconnected until the liquid pressures equalize; otherwise the liquid may surge up and wet the asbestos plug. If this occurs, it must be discarded, the bore dried and repacked and the new plug calibrated.

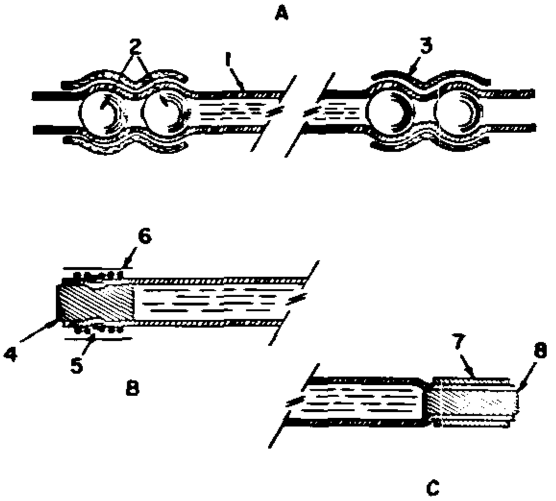
This device is a very convenient and precise method for metering low flows in the indicated range. The output flow remains constant for weeks, but should be checked occasionally. The delivery tip is connected to the mixer shown in Figure 12-3. For low delivery rates, the dead volume is minimized by using capillary tubing.

The levelling bulb vent is connected to a tap on the diluted gas manifold. This provides a correction for back pressure of the system into which the flow is being delivered. An appreciable back pressure changes the pressure differential across the asbestos plug. The bulb vent connection causes the liquid level to rise in the vent tube. If the vent area is small compared to the area of the liquid surface in the bulb, this compensates almost exactly for the back pressure by increasing the upstream pressure on the plug enough to maintain a constant pressure differential.

Permeation Tubes

Permeation tubes are very useful sources for liquifiable gases. Because of their potential precision, recent collaborative tests of methods have employed them when applicable. The National Bureau of Standards now certifies the sulfur dioxide type. Because of their importance as primary standards, they are described below in some detail.

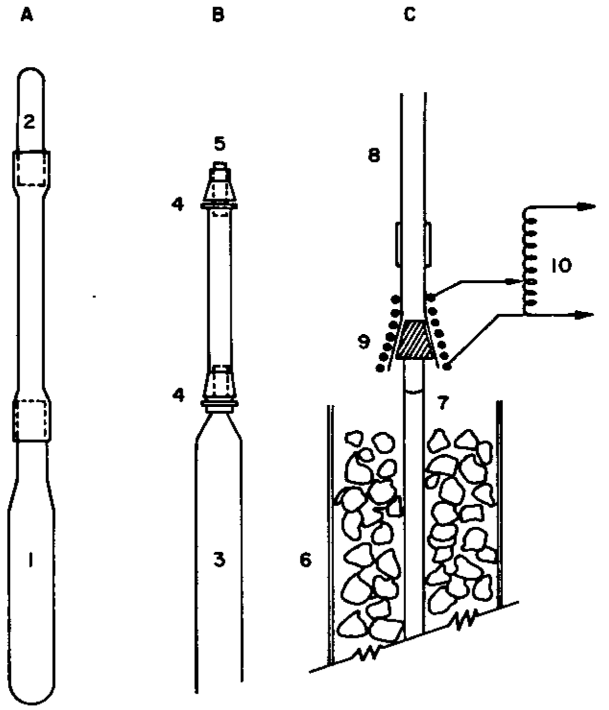
In these devices the liquid is sealed under pressure in inert Teflon tubes. The vapor pressure may be as high as 10 atmospheres. The gas permeates out through the walls of the tube at a constant rate of a few milligrams per day for periods as long as a year. Figure 12-10 illustrates three types of seals: steel or glass balls, a Teflon plug bound with wire and a Teflon plug held by a crimped metal band. Figure 12-11 shows some other types of seals and construction. In order to extend the lifetime of some tubes, a glass or stainless steel bottle containing the liquified gas may be attached to the Teflon tubing, as shown in Figure 12-11A or B. At low pressure, such as in permeation tubes containing nitrogen dioxide (b.p. 21.3°C), a sufficiently tight seal may be obtained by pushing the Teflon tube onto the neck of the glass bottle and by pushing a glass plug in at the top. For higher pressures, such as in tubes containing propane (vapor pressures 10 atm. at 25°C), a stainless steel bottle is used, as shown in Figure 12-11B. The seals are made by crimping ¼" Swagelok ferrules on the ends of the Teflon tube. Another type of seal is illustrated in Figure 12-11C in which a FEP Teflon plug is fused to a FEP Teflon tube by means of heat.



International Symposium on Identification and Measurement of Environmental Pollutants, c/o National Research Council of Canada, Ottawa, Ontario, Canada, 1971.

Figure 12-10. Three Types of Seals: (1) Steel on Glass Balls, (2) a Teflon Plug Bound with Wire, and (3) a Teflon Plug Held by a Crimped Metal Band

All tubes, especially if the contents are under pressure, should be handled with caution. If they have been chilled in dry ice during filling, room for expansion of the liquid upon warming to ordinary temperatures should be provided. Tubes should be protected from excessive heat. They should not be scratched, bent, or mechanically



Env. Sci. Tech. 5:1121, 1971.

Figure 12-11. A & B. A Glass or Stainless Steel Bottle Attached to Teflon Tubing
Figure 12-11C. An FEP Teflon Plug Fused to an FEP Teflon Tube

abused. After a new tube has been prepared, several days or weeks are required before a steady permeation rate is achieved at a thermostated temperature. Saltzman, Burg, et al.[17] reported that tubes made of FEP Teflon should be annealed at 30°C for a period in order to equilibrate the Teflon and achieve a steady rate. Otherwise, a pseudo-stable rate is achieved which is not reproduced after appreciable temperature fluctuations.

Gravimetric calibrations may be made by weighing the permeation tubes at intervals and plotting the weight against time. The slope of the line fitted by the method of least squares to the measured points is the desired rate. This process may take as long as several weeks with an ordinary balance because of the necessity of waiting to obtain measurable weight differences. However, if a good micro balance is available, the calibration can be shortened to a day. Static charges which develop on some permeation tubes can cause serious weighing errors unless discharged with a polonium strip static eliminator. For a corrosive gas, the balance may be protected from corrosion by inserting the permeation tubes into glass-stoppered weighing tubes. The weight history of a nitrogen dioxide tube over a 37 week period is shown in Figure 12-12. The tubes are used by passing a metered air flow over them in a vessel thermostated to ± 0.1°C, as illustrated in Figure 12-13. Close temperature control is essential because the temperature coefficient is high.

A relatively inexpensive apparatus may be used for volumetric calibration purposes[16,17] which makes possible a calibration in less than an hour. A Gilmont Warburg compensated syringe manometer measures the evolved gas from a permeation tube with a sensitivity of 0.2 microliter.

Exposures of some types of permeation tubes must be very carefully controlled. Thus, nitrogen dioxide tubes exposed to high humidity develop blisters and long term changes in permeation rates; even the moisture content of the flowing gas passing over the tube affects the rate. These effects are likely due to the formation of nitric acid within the Teflon walls and/or inside the tube in the liquid nitrogen dioxide. A similar problem occurs with hydrogen sulfide tubes, which precipitate colloidal sulfur within the walls of the tube when exposed to oxygen. It is therefore desirable never to remove such tubes from their operating environments. Figure 12-14 illustrates a system which accomplishes this. A slow stream (50 ml/min.) of dry nitrogen from a cylinder is passed over the tube to flush away the permeated gases. This stream can be blended with a metered pure air flow in a flow dilution system to produce known concentrations of the gas. When calibration is desired, the gas flow from the nitrogen cylinder is temporarily shut down and a volumetric calibration performed within an hour or so. High precision has been obtained in this manner.

The quantitative relationships for permeation through a tube of unit length are given[16] by equation 5:

$$G = 730\ P \times M.W. \times p_1/\log(d_2/d_1) \quad (5)$$

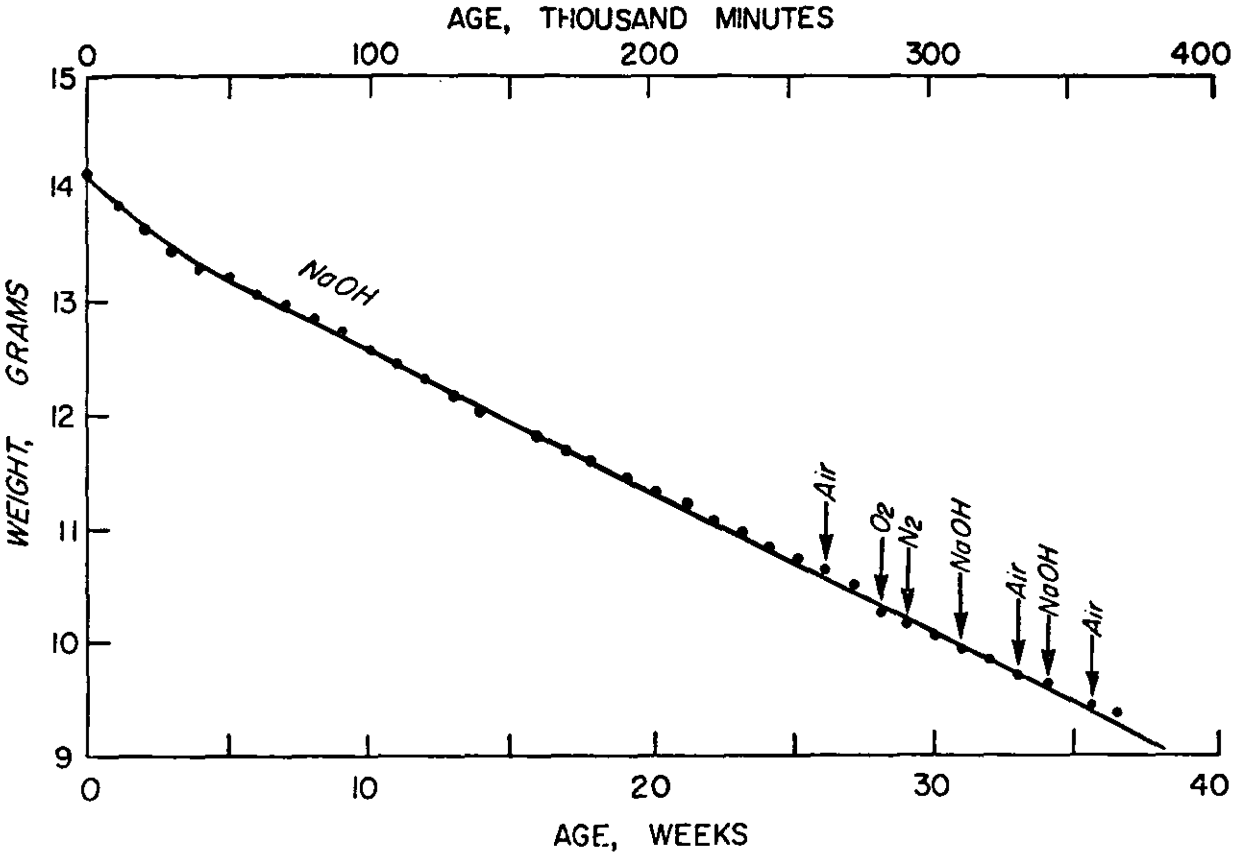
where G = mass permeation rate, μg/min. per cm of tube length
P = permeation constant for the gas through the plastic, in cc(STP) cm/cm^{2}sec(cm Hg)
M.W. = molecular weight of gas
d_2 = outside diameter of tube
d_1 = inside diameter of tube
p_1 = gas pressure inside tube, mm Hg
log = logarithm to base 10

The permeation rates have high temperature coefficients. Equation 6 shows the usual relationship in the form of the Arrhenius equation.

$$\log\left(\frac{G_2}{G_1}\right) = \frac{E}{2.303\ R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (6)$$

where G_1, G_2 = gravimetric rates at different temperatures
T_1, T_2 = corresponding temperatures, °K (= °C + 273.16)
E = activation energy of permeation process, cal/g mol
R = gas constant, 1.9885 cal/g mol °K

Table 12-2 lists permeation rates for various tubes, some of which are commercially available, together with some data for activation energies.



Env. Sci. Tech. 5:1121, 1971.

Figure 12-12. Weight History of a Nitrogen Dioxide Tube over a 37-Week Period

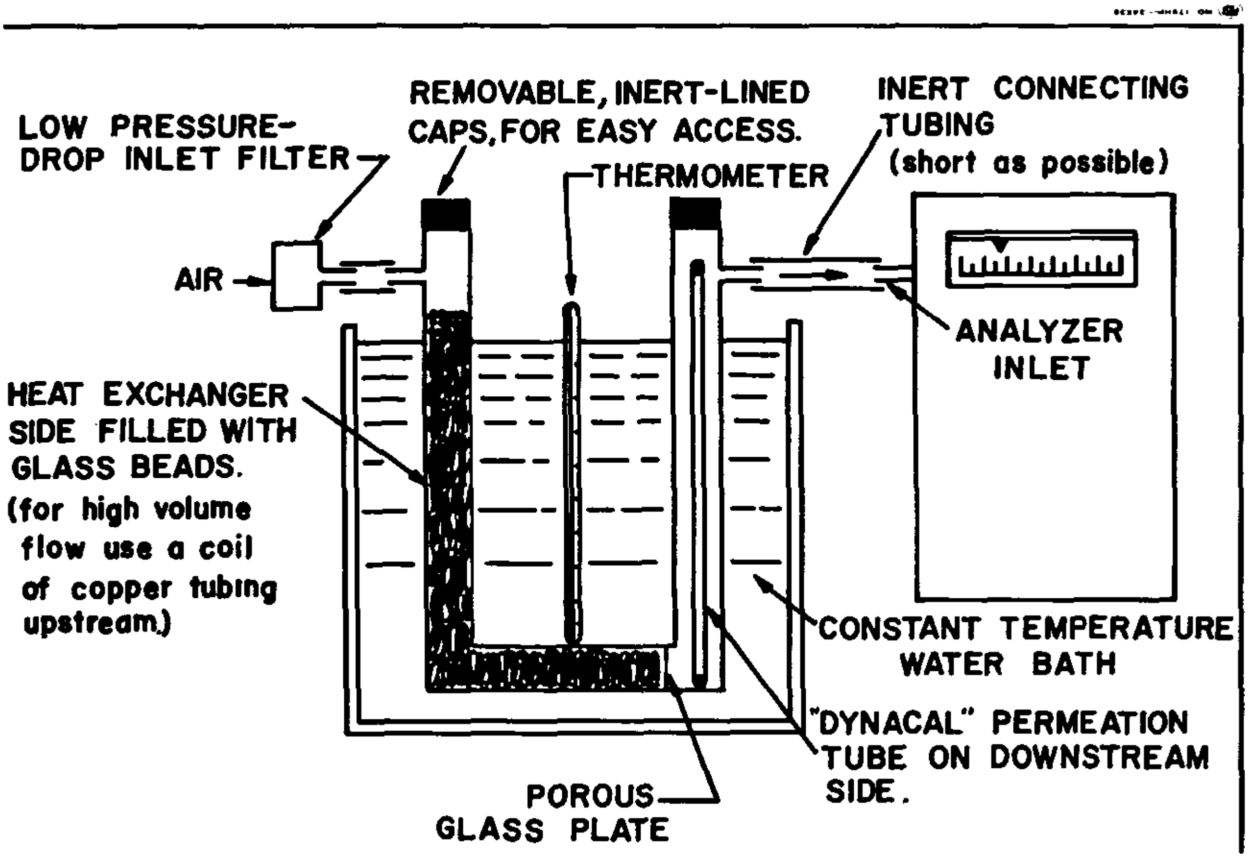
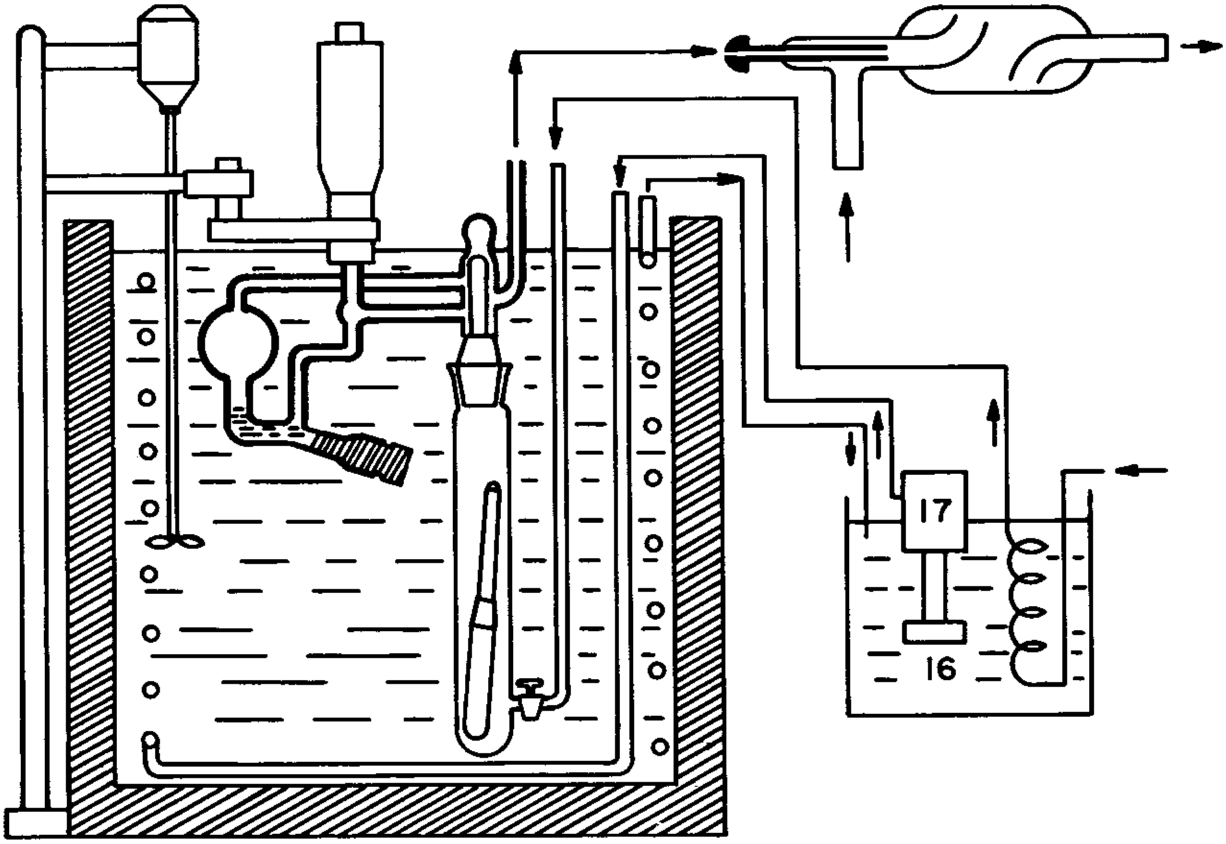


Figure 12-13. Passage of a Metered Air Flow over Tubes



Env. Sci. Tech. 5:1121, 1971.

Figure 12-14. A System Never Requiring Removal of Tubes From Their Operating Environment

Table 12-2

PERMEATION RATES FOR SOME TEFLON PERMEATION TUBES[16]

Rates are in ug/min. cm

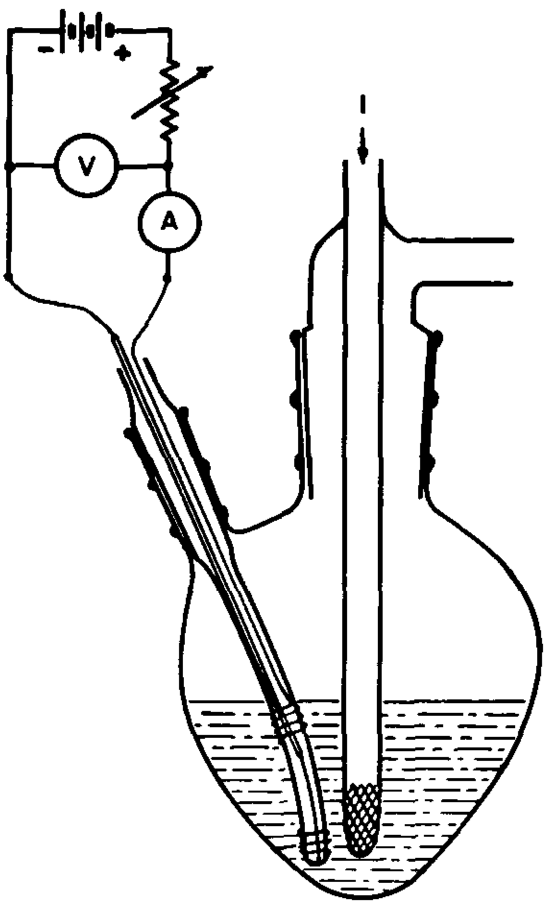
Activation Energies, E, are in Kcal/g. mol

	Dynacel Tubes[a]		*A.I.D. Tubes*[b]	*FEP Teflon*[c]		*TFE Teflon*[c]	
Substance	*Rate*	*E*	*Rate*	*Rate*	*E*	*Rate*	*E*
SO_2	0.422	13.8	0.279				
NO_2	1.714	14.7	1.230	2.09	14.6		
HF	0.185						
H_2S	0.457	16.0	0.229				
Cl_2	2.418	14.0	1.430				
NH_3	0.280		0.165				
CH_3SH	0.036	10.0	0.030				
Propane	0.080	15.0	0.035	0.132	16.2	1.86	13.0
Propene	0.240			5.13	15.4		
n Butane			0.012	0.024	15.8	0.258	12.7
Butene-1				0.0316	14.8	0.368	12.4

[a] Available from Metronics Associates, Inc., Palo Alto, Calif. 94304. Tubes are 3/16″ O.D., ⅛″ I.D. Rates are at 30°C.

[b] Available from Analytical Instrument Development, Inc., West Chester, Pa. 19380. Tubes are FEP Teflon, 0.250″ O.D. and 0.062″ wall thickness except for methyl mercaptan, which is 0.030″ wall thickness. Rates are at 30°C.

[c] 0.250″ O.D. and 0.030″ wall thickness, as reported by Saltzman et al.[17] Rates are at 25°C.



Anal. Chem. 33, 1100, 1961.

Figure 12-15. Electrolytic Generator

Miscellaneous Generation Systems

Figure 12-15 illustrates an electrolytic generator that was developed[1] as a suitable source of arsine and stibine. The solution is electrolyzed by passing a DC current through the platinum wire electrodes (0.41 mm diameter x 3 cm long) shown in the figure. The lower electrode is the cathode at which hydrogen and small quantities of arsine or stibine are liberated. The stream of purified air bubbles through the fritted tube end near the cathode and flushes the gas mixture into the outlet. At low current densities there was an appreciable time lag before arsine or stibine appeared. The generation rate of arsine or stibine was not proportional to the current but was accelerated at higher currents. To achieve high current densities wire electrodes rather than plates were used.

Another system used successfully was an aerated chemical solution mixture.[1] Thus, a 30% w/v solution of potassium cyanide served as a source of hydrogen cyanide. A relatively constant concentration could be obtained for as long as 10 hours. The strength and pH of the solution affected the concentration of hydrogen cyanide produced. The air bubbled through the solution should be free from carbon dioxide, since carbonic acid can displace hydrogen cyanide. Because the dissolved salt tended to crystallize at the air inlet and plug it, the aeration was stopped every hour for a few moments to allow the solution to re-enter the inlet and redissolve the accumulated salt. In another application, hydrogen chloride was obtained by aeration of a 1 : 1 concentrated hydrochloric acid-water mixture. Bromine was obtained by aerating saturated bromine water in contact with a small amount of liquid bromine. In all of these procedures it is, of course, desirable to thermostat the bubbler to provide constant concentrations.

An interesting technique for preparing highly reactive or unstable mixtures is to utilize chemical conversion reactions. A stable mixture of a suitable compound is passed over a solid catalyst or reactant to produce the desired substance in the air stream. A table of reactions presented by Hersch[3] indicated some of these possibilities. Others may be determined from the literature. Multistep conversions also may be utilized.

SOURCE DEVICES FOR AEROSOLS

Introduction

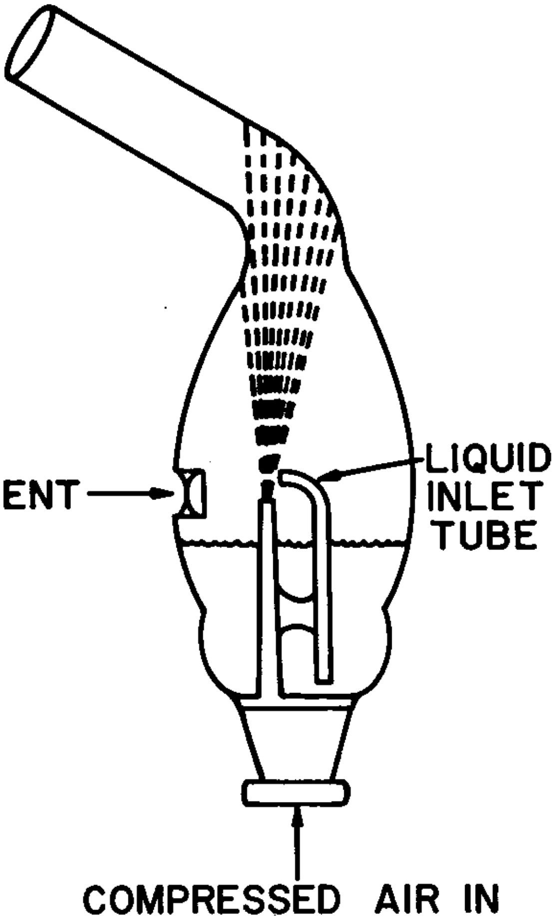
Preparation of aerosol mixtures is much more complex and difficult than that of gas and vapor mixtures. A major consideration is the size distribution of the particles. Commonly a log normal distribution describes the values; this is characterized by a geometric mean and a standard geometric deviation. The usual aerosol source device supplies a range of sizes. However, certain special types supply uniform-sized particles. If the standard geometric deviation is less than 1.1, the particles are considered homogeneous, or monodisperse. There is also a great variety of particular shapes, including spherical, crystalline, irregular, plate-like, spiked, and rod-shaped or fibrous. If the material is a mixture of compounds, the composition may vary with size. Certain substances may be present on the surfaces, which also can be electrostatically charged. All of these properties are affected by the source devices and the methods of treatment. In the generation of known concentrations of aerosols, the choices of the operating parameters are determined by the objectives of the study, which may be to duplicate and study a complex aerosol existing naturally or in industry, or to prepare a simple pure aerosol for theoretical examination. A good general treatment of this subject with 257 references was published by Raabe.[18]

Dry Dust Feeders

A comprehensive description of methods of producing solid aerosols was given by Silverman and Billings.[19] One of the most convenient and widely used methods is to redisperse a dry powder. Standard test dusts are available, such as road dust, fly ash, silicates, silica, mineral dust and many pigment powders and chemicals. Because these may tend to agglomerate, the degree of packing of the powder must be controlled and reproducible. A simple method consists of shaking the powder on a screen into the air stream. Mechanical systems attempt to provide a constant feed rate by use of moving belts or troughs, or by rotating turn tables, screws or gears. Because of the erratic behavior of loosely packed dust, the popular Wright dust feed mechanism achieves closer control by compressing the dust in a tube into a uniform cake. A rotating scraper advanced by a screw slices off a thin layer of the cake continuously. In all of these devices the dust is dispersed by an air jet, which also serves to break up some aggregates. The dusty cloud is passed into a relatively large chamber, which serves to smooth out any rapid fluctuations. Concentrations may fluctuate ± 20% over a period of a half hour, due to variations in the packing of the dust or laminations in the cake. Settling chambers, baffles, or cyclones may be added to the system to remove coarse particles, and ion sources to remove electrostatic charges.

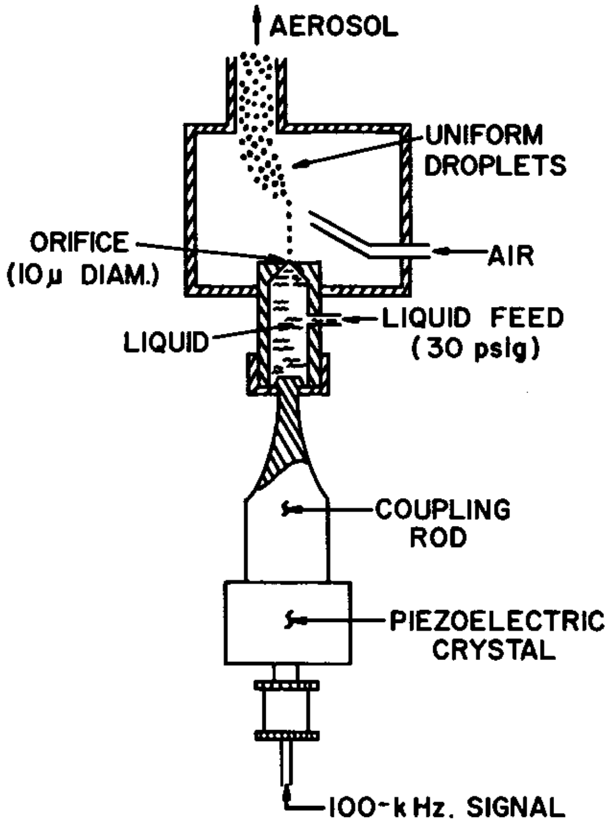
Nebulizers

The compressed air nebulizer, Figure 12-16, is a convenient and useful device to produce aerosols from liquids. The liquid stream is drawn through a capillary tube and shattered into fine droplets by the air jet. The DeVilbiss nebulizer is simple, but holds only about 10 ml of liquid. Modifications can be added,[18] such as utilizing a recirculating reservoir system for the liquid (Lauterbach), providing baffles to intercept and return coarse droplets (Dautrebande), droplet shattering baffles (Lovelace) and nozzle controls. The characteristics of these devices have been described in detail.[20]



Amer. Ind. Hyg. Assoc. J. 29.66, 1968.

Figure 12-16. Compressed Air Nebulizer



Inhalation Carcinogenesis, April 1970 (CONF0691001, AEC Symposium Series 18).

Figure 12-17. Ultrasonic Droplet Generator

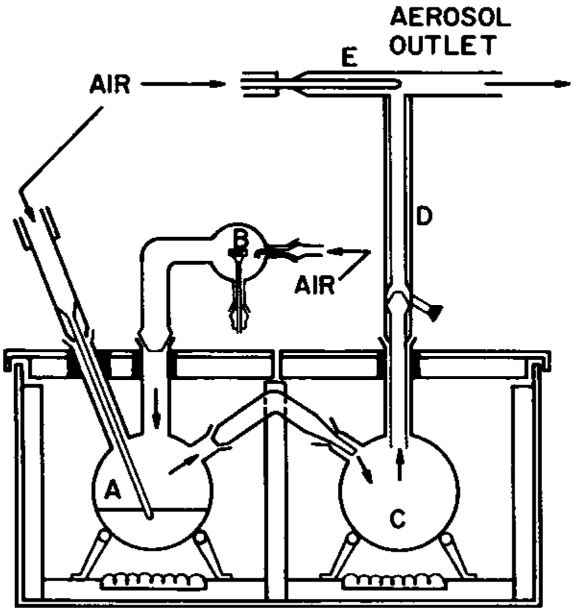
Rather coarse sprays are obtained by pumping the liquid mechanically through tangential nozzles, as is done in fuel oil burners. The air flow merely carries off the droplets. Somewhat different is the ultrasonic droplet generator, Figure 12-17, which utilizes an intense acoustic field to produce fine droplets. In the version illustrated the pressurized liquid is ejected from the orifice as a fine stream, which is disrupted by the vibrations of the coupling rod into remarkably uniform-sized droplets (coefficient of variation < 1%).

Commercial aerosol cans utilize a mixture of liquid to be atomized and a volatile propellant (usually a Freon compound such as dichlorodifluoromethane). The rapid evaporation of the propellant from the liquid emerging from the nozzle orifice shatters the stream into droplets having a broad size range. Electrostatic dispersion also has been utilized to break up a liquid stream by electrically charging the orifice. The droplets should be discharged by passage near an ion source soon afterwards.

These liquid sources can be readily applied to supply solid aerosols by dispersing a solution or colloidal suspension. The solvent evaporates from the droplets naturally or upon warming, leaving a smaller particle of crystalline solute, or a clump of one or more colloidal particles according to their theoretical probabilities of occurrence in the volume of the droplet. The nature of the materials and of the drying process often affects the nature of the particles, which may exhibit shells or crusts. Passing the particles through a high temperature zone may be employed to chemically decompose them (e.g., production of metal oxides from their salts) or to fuse them into spherical particles.

Vaporization and Condensation of Liquids

The principle of vaporization and condensation was utilized in the Sinclair-LaMer generator for materials such as oleic acid, stearic acid, lubricating oils, menthol, dibutyl phthalate, dioctyl phthalate and tri-o-cresyl phosphate, as well as for sublimable solids. The system is illustrated in Figure 12-18 (from Fuchs and Sutugin — see Preferred Reading). Filtered air or nitrogen is bubbled through the hot liquid in the flask on the left. Another portion of the entering air is passed over a heated filament coated with sodium chloride, to provide fine condensation nuclei. The vapor passes into the empty superheater flask on the right, in which any droplets are evaporated, and then up the chimney in which it is slowly cooled. The supersaturated vapor condenses on the sodium chloride particles to produce a monodisperse aerosol. Although the condensation nuclei vary in size they have only a slight effect on the final aerosol droplet size, which is much larger. This system has been widely utilized as a convenient monodisperse source in the 0.02 to 30 micron size range.



Davies CN (ed): Aerosol Science. New York, Academic Press, 1966.

Figure 12-18. Sinclair LaMer Generator

Spinning Disc Aerosol Generators

A very useful generator for monodisperse aerosols is based upon feeding the liquid continuously onto the center of a rapidly spinning disc (60,000 rpm). When the droplet on the edge of the disc grows to a sufficient size, the centrifugal force exceeds that of surface tension and the droplet is thrown off. A commercial system, illustrated in Figure 12-19, produces liquid droplets in the 1 to 10 micron size range. Smaller satellite drops are diverted down by an air stream into a compartment around the disc. The larger particles escape to the outer compartment, and are passed around a sealed radioactive ion source to remove the electrostatic charges, then to the outlet. Solid particles also can be generated from solutions and suspensions. The sizes are controlled by varying the concentrations.

Miscellaneous Generation Systems

Many dusts can be produced by means duplicating their natural formation. Thus, hammer or impact mills, ball mills, scraping, brushing and grinding of materials have been employed. Combustion (e.g., tobacco smoke), high voltage arcing, and gas welding or flame cutting torches can be used. Organic metallic compounds (e.g., lead tetraethyl) may be burned in a gas flame. Metal powders can be fed into a flame, or burned spontaneously (thermit and magnesium). Molten metals may be sprayed from metallizing guns. Metal wires can be vaporized by electrical discharges from a bank of condensers. A fluidized bed may be utilized as a reproducible source of particulate material. Gaseous reactions also may be employed to produce aerosols, such as reaction of sulfur trioxide with water vapor, or of ammonia and hydrogen chloride. Finally, photochemical reactions can be utilized. The natural process for producing oxidative smog has thus been duplicated by irradiating automobile exhaust.

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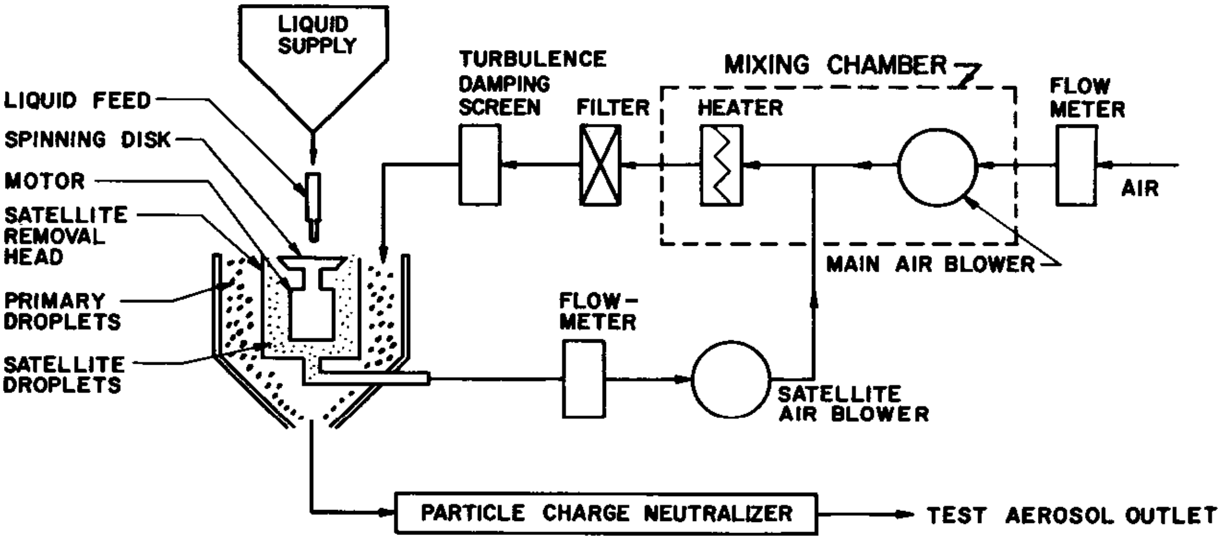

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Figure 12-19 Spinning Disc Aerosol Generator

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