

CHAPTER 12

PREPARATION OF KNOWN CONCENTRATIONS OF AIR CONTAMINANTS

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INTRODUCTION

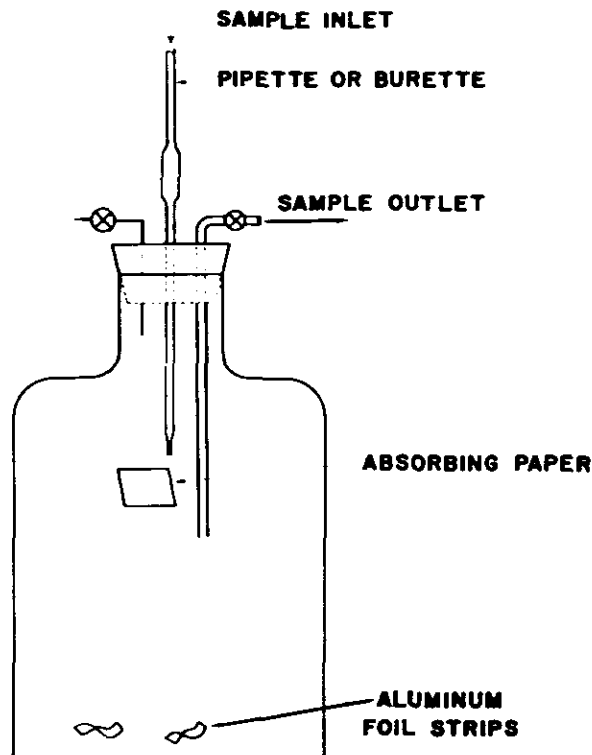
Known low concentrations of air contaminants are required for many purposes. There has been a technical explosion in recent years in the development of a great variety of monitoring instruments for measuring concentrations of air contaminants, based upon electronic means. These devices are invaluable; 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.^{4,5} 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.

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

Where C = final concentration in bottle or chamber

C_0 = initial concentration

W = volume withdrawn, liters

V = original volume of mixture, liters

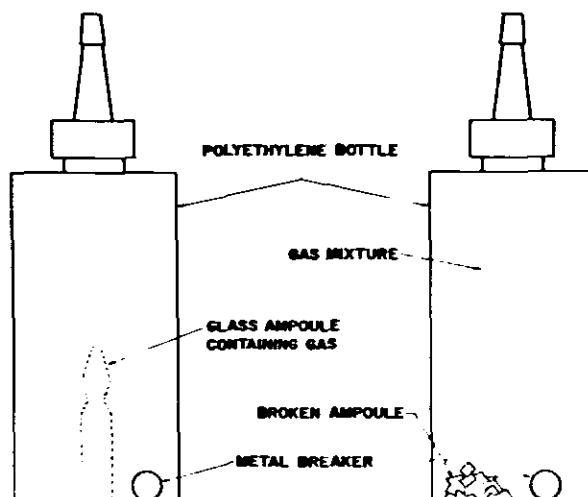
Some calculated values are shown in Table 12-1.

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 ampoule 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 mix-



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

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

ture. These devices are relatively simple, convenient and sufficiently accurate for this purpose.

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 Schuette⁹ 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 study¹⁰ 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.

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

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.

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

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

where w = weight of volatile liquid introduced, grams

M.W. = gram molecular weight of liquid
 \bar{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:

$$\text{M.W. of } \text{CCl}_4 = 12.01 + 4 \times 35.457 = 153.84$$

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

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

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 pro-

portional 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.

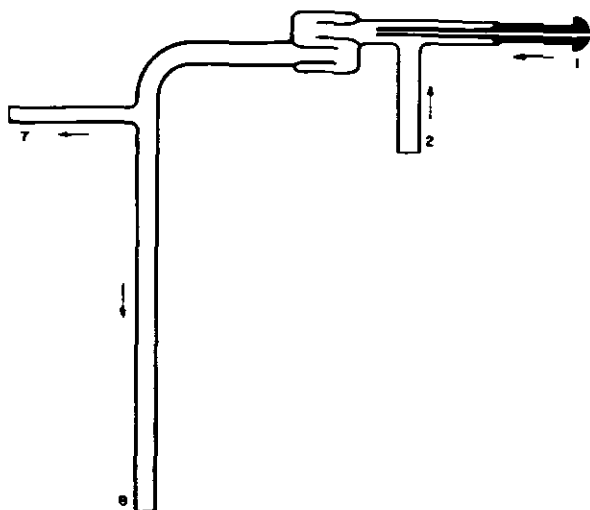
There are two types of corrections of flow meter calibrations for ambient pressure and temperature. The first is the correction to the actual flow because of the fact that the measured value is dependent upon the density and in some cases the viscosity of the gas flow, both of which are affected by ambient 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.

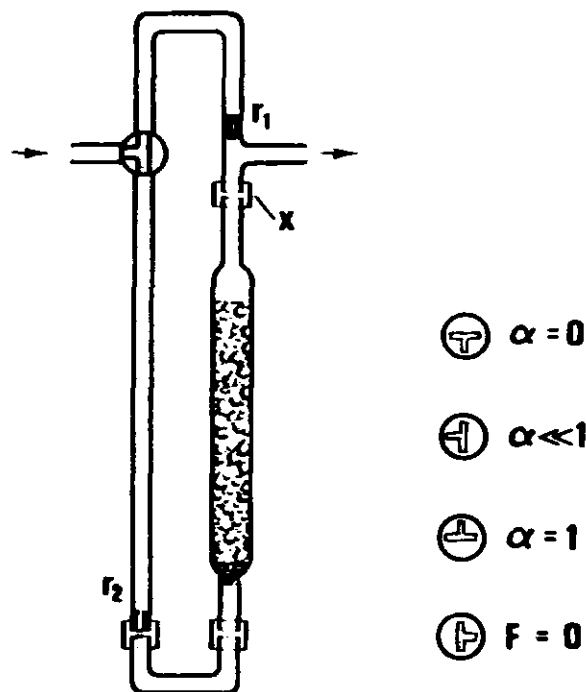
The dilution air must be purified according to the needs of the work. Air can be passed over a bed of carbon, silica gel, or ascarite, or bubbled through a scrubbing mixture of chromic acid in concentrated sulfuric acid if necessary. Another convenient method of purification is to pass the air flow through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



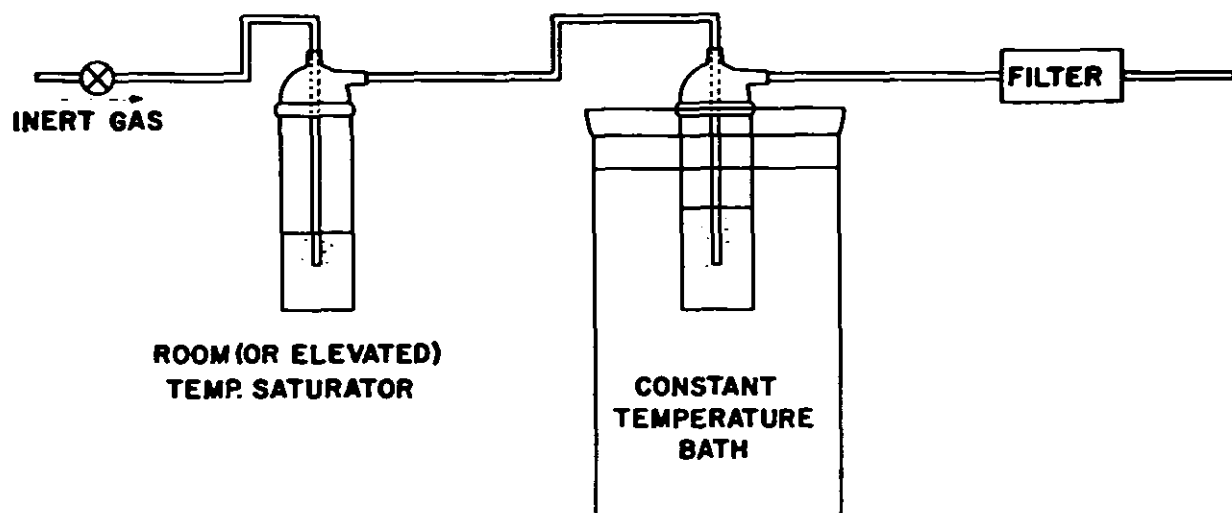
J. Air Pollution Control Assoc. 19:164, 1969.

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



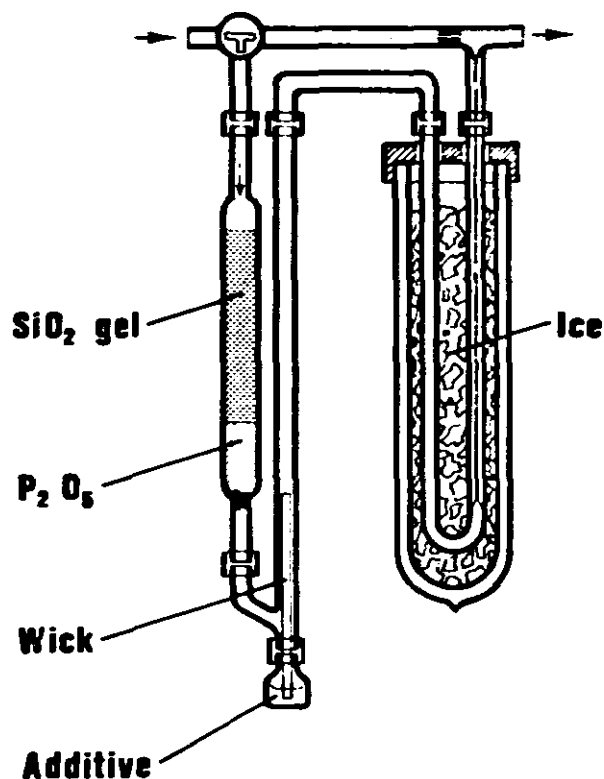
Amer. Ind. Hyg. Assoc. J. 22:392, 1966.

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



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

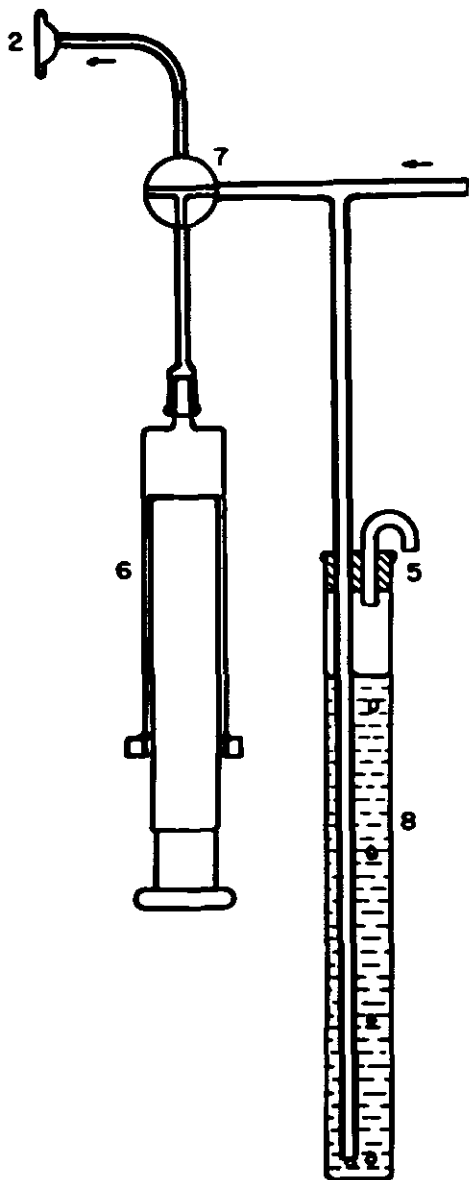
Figure 12-6. Vapor Saturator

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.

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.⁽¹²⁾

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.

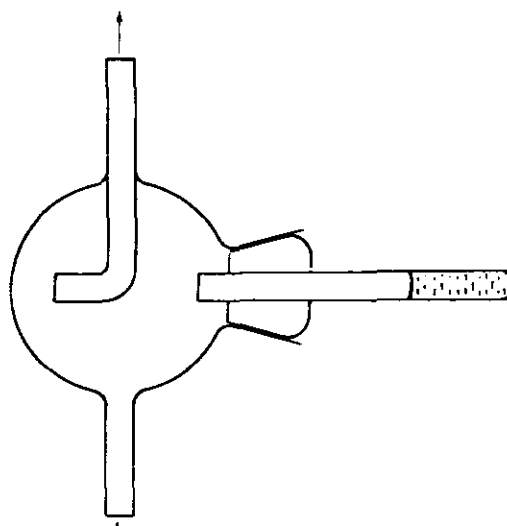


Figure 12-8. Diffusion System

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

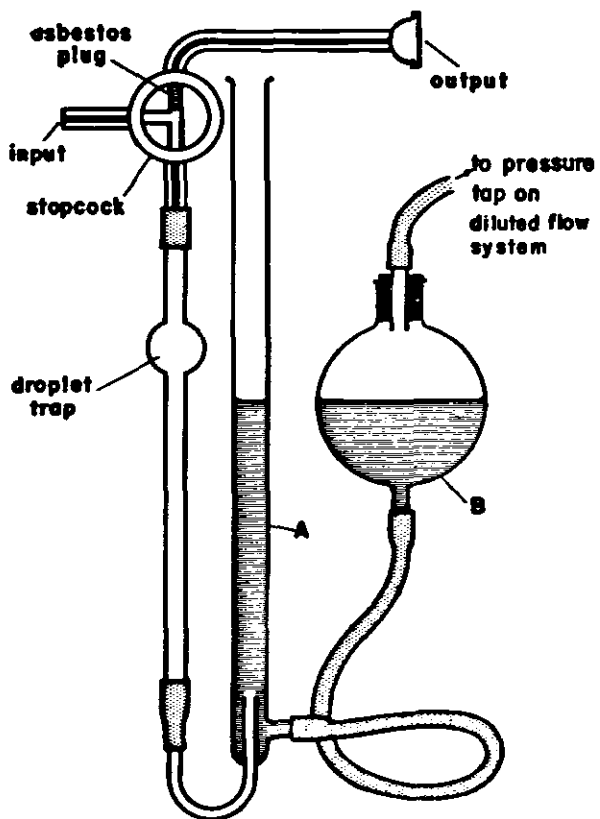


Figure 12-9. Micrometering System

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.

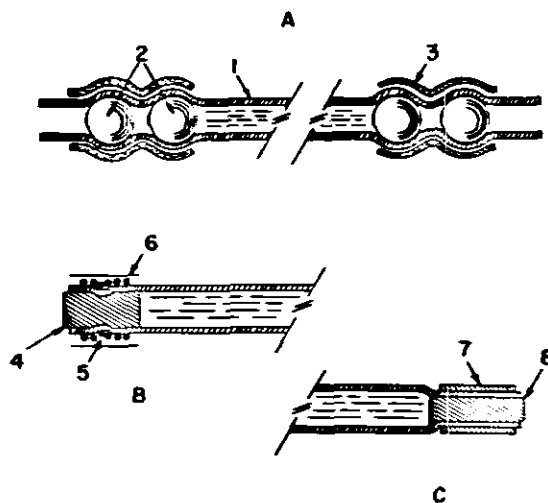
The levelling bulb vent is connected to a tap on the diluted gas manifold. This provides a correction for back pressure of the system into which the flow is being delivered. An appreciable back pressure changes the pressure differential across the asbestos plug. The bulb vent connection causes the liquid 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

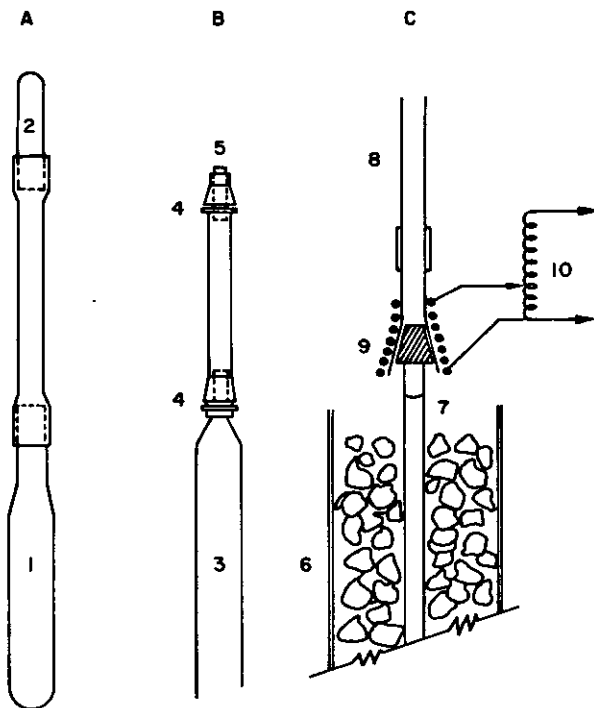


International Symposium on Identification and Measurement of Environmental Pollutants, c/o National Research Council of Canada, Ottawa, Ontario, Canada, 1971.

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

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.

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 $\pm 0.1^\circ\text{C}$, 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 given¹⁶ by equation 5:

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

where G = mass permeation rate, $\mu\text{g}/\text{min.}$ per cm of tube length

P = permeation constant for the gas through the plastic, in $\text{cc}(\text{STP}) \text{ cm}/\text{cm}^2\text{sec}(\text{cm Hg})$

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.

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

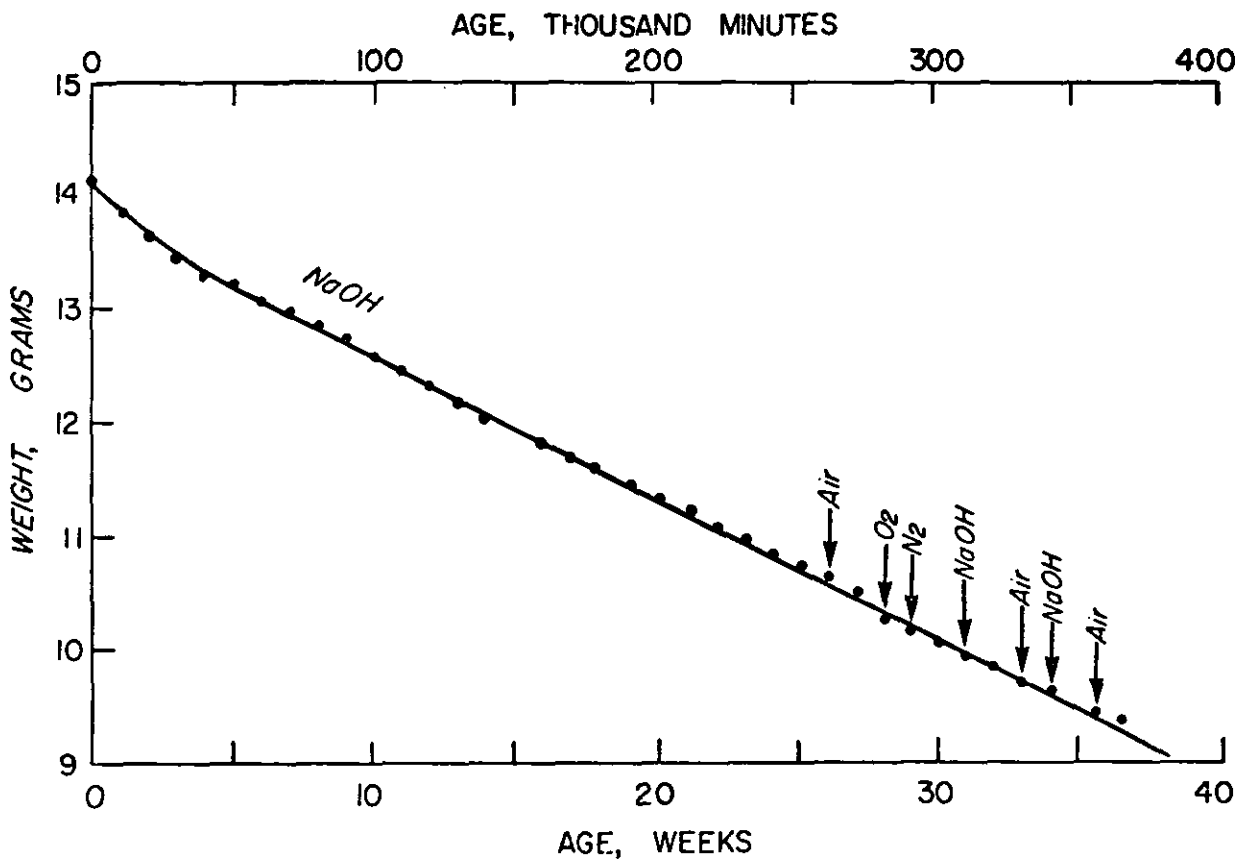
where G_1, G_2 = gravimetric rates at different temperatures

T_1, T_2 = corresponding temperatures, $^\circ\text{K}$ ($= ^\circ\text{C} + 273.16$)

E = activation energy of permeation process, $\text{cal}/\text{g mol}$

R = gas constant, $1.9885 \text{ cal}/\text{g mol } ^\circ\text{K}$

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

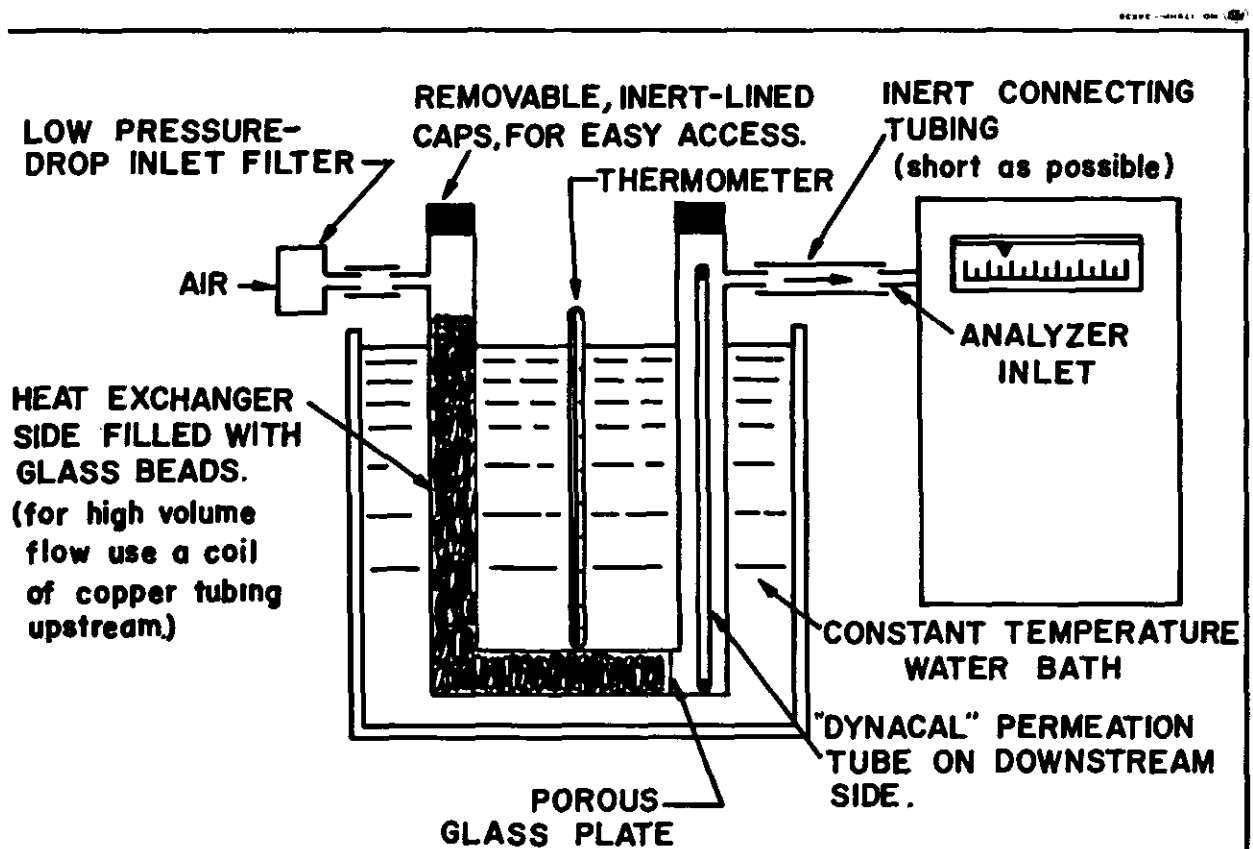
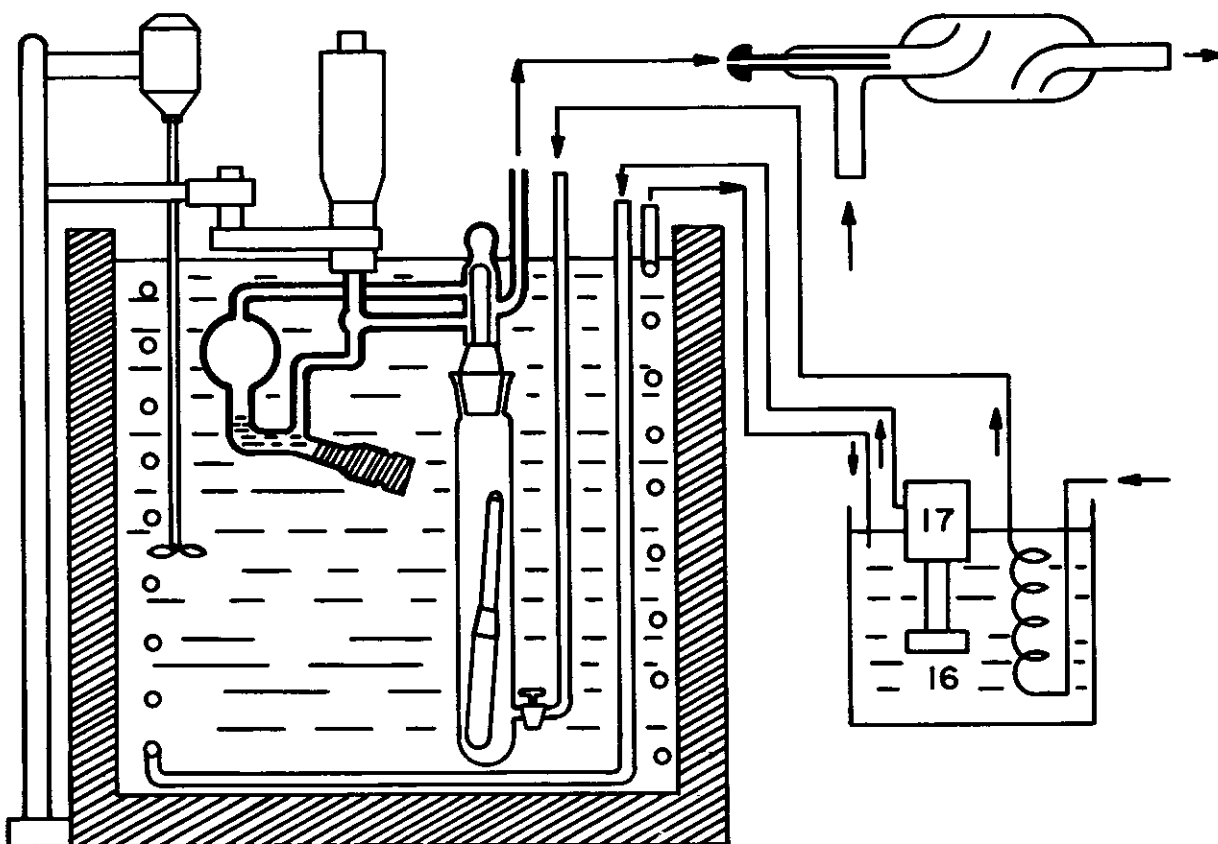


Figure 12-13. Passage of a Metered Air Flow over Tubes



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 TUBES¹⁶

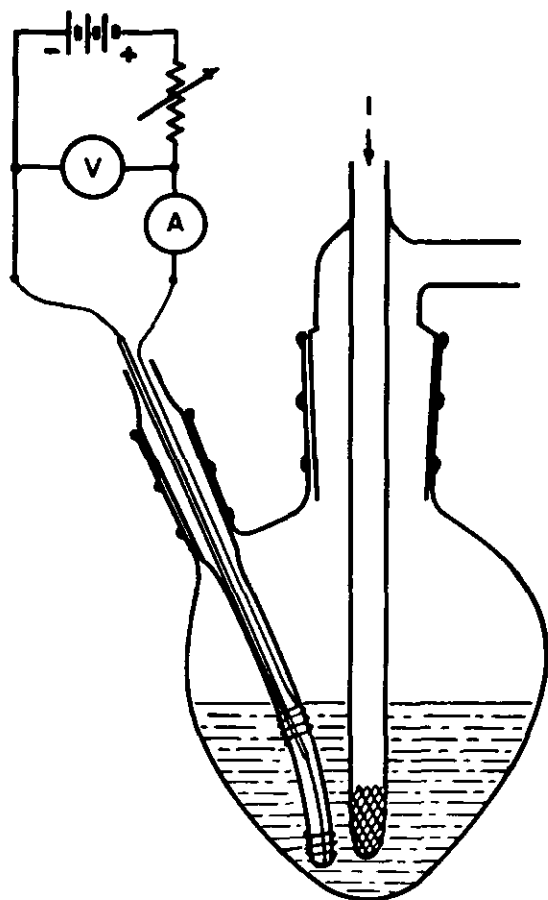
Rates are in ug/min. cm
Activation Energies, E, are in Kcal/g. mol

Substance	Dynacel Tubes ^a		A.I.D. Tubes ^b	FEP Teflon ^c		TFE Teflon ^c	
	Rate	E		Rate	Rate	E	Rate
SO ₂	0.422	13.8	0.279				
NO ₂	1.714	14.7	1.230	2.09	14.6		
HF	0.185						
H ₂ S	0.457	16.0	0.229				
Cl ₂	2.418	14.0	1.430				
NH ₃	0.280		0.165				
CH ₃ SH	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., 1/8" 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 developed¹ 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 Hersch² 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

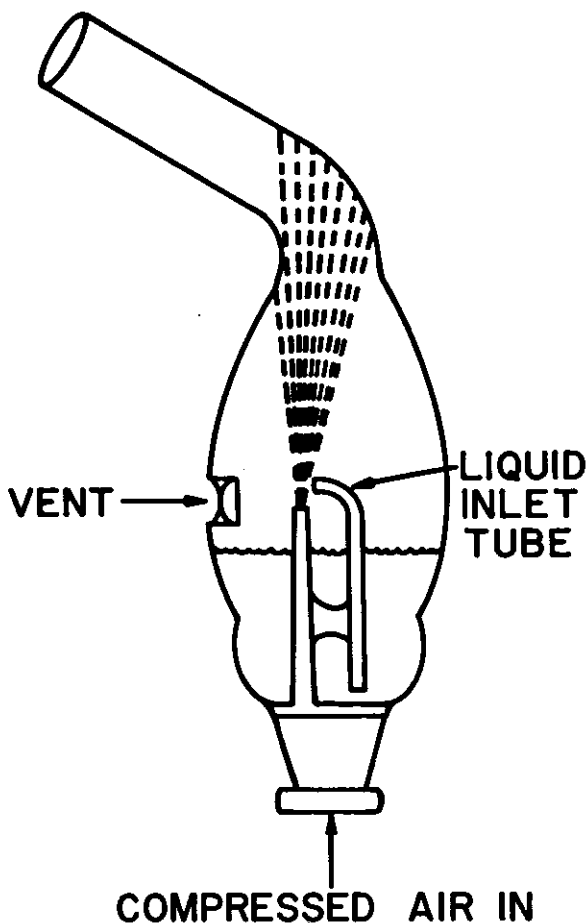
Dry Dust Feeders

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 $\pm 20\%$ 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.

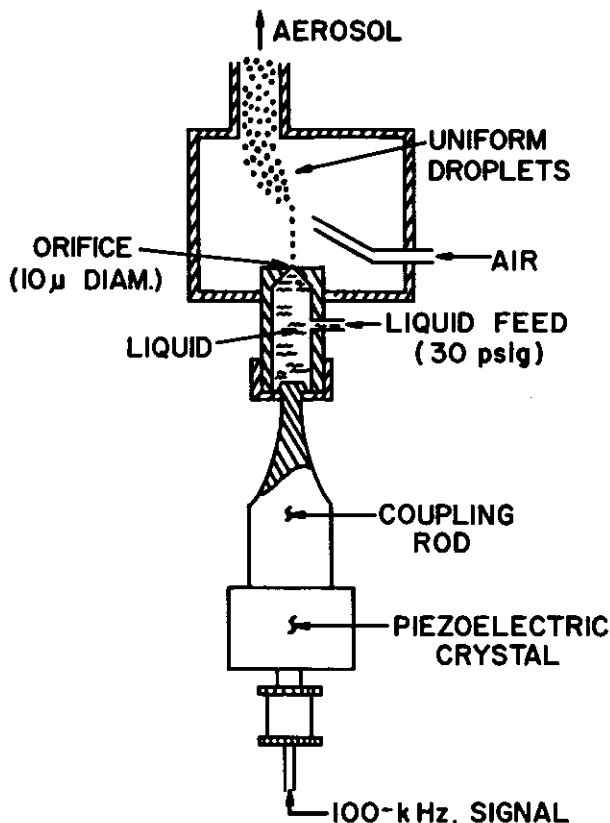
Nebulizers

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



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

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

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 $< 1\%$).

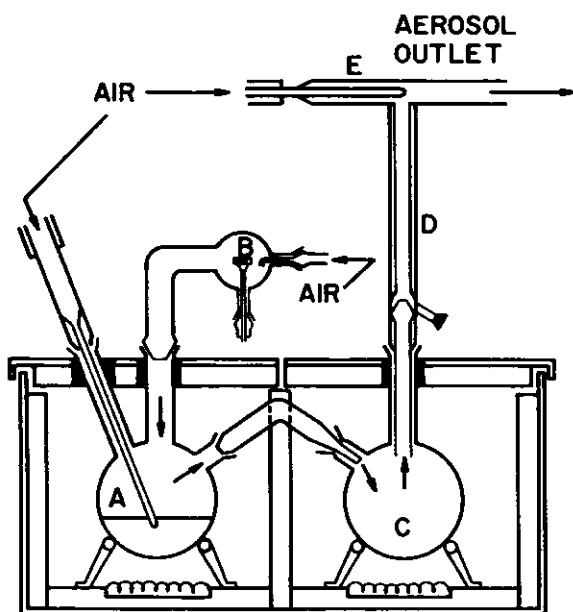
Commercial aerosol cans utilize a mixture of liquid to be atomized and a volatile propellant (usually a Freon compound such as dichlorodifluoromethane). The rapid evaporation of the propellant from the liquid emerging from the nozzle orifice shatters the stream into droplets having a broad size range. 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



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

Figure 12-18. Sinclair LaMer Generator

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.

Spinning Disc Aerosol Generators

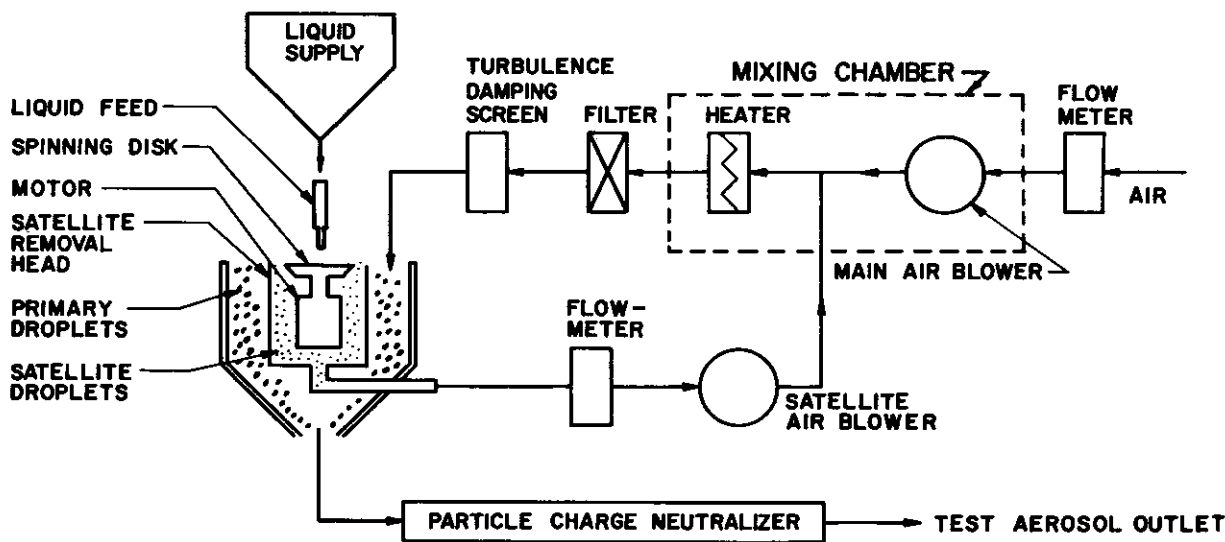
A very useful generator for monodisperse aerosols is based upon feeding the liquid continuously onto the center of a rapidly spinning disc (60,000 rpm). When the droplet on the edge of the disc grows to a sufficient size, the centrifugal force exceeds that of surface tension and the droplet is thrown 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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Figure 12-19 Spinning Disc Aerosol Generator

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SAMPLING AIR FOR PARTICULATES

S. A. Roach, Ph.D.

INTRODUCTION

The particulates of significance to industrial hygienists include all particles, solid or liquid, which are suspended in air and may be inhaled. The particles may be of all sizes from molecular dimensions up to about 100 microns in diameter. The three main types of particulates are dust, mist and fume.

Primary Airborne Dust

Primary airborne dust consists of solid particles rendered airborne during the crushing, grinding or attrition of hard, rock-like materials. Dust particles generally have irregular shapes.

Secondary Airborne Dust

Secondary airborne dust is produced by dispersion into the air of fine powder from a bulk source or from previously settled primary airborne dust. Airborne particles, on close examination, are often found to consist of clumps or aggregates of smaller particles adhering together.

Mist

A mist is formed from a material which is liquid at room temperature. Mist particles are the airborne droplets rendered airborne by bubbling, boiling, spraying, splashing or otherwise agitating a liquid and also by condensation from air super-saturated with the vapor of the substance. Mist particles are generally spherical in shape.

Primary Fume

A fume is formed from a material which is solid at room temperature. Fume, like certain mist formations, is produced by condensation from air super-saturated with the vapor of the material. More commonly, fume is the airborne solid particulate formed in the air above molten metal, by vaporization of the metal, oxidation of the vapor and condensation of the oxide. Fume particles generally have irregular shapes.

Secondary Fume

Secondary airborne fume is produced by dispersion into the air of fume from a bulk source or by redispersion of settled primary fume. The airborne particles of secondary fume are almost always much coarser than those of the primary type, consisting of clumps of innumerable, very fine particles.

Sampling is performed by drawing a measured volume of air through a filter, impingement device, electrostatic or thermal precipitator, cyclone or other instrument for collecting particulates. The concentration of particulate in air is denoted by the weight or number of particles collected per unit volume of the air sample. The weight of collected material is determined by direct weighing or by chemical analysis, as appropriate.

The number of particles collected is determined by counting the particles in a known portion of the sample. This is accomplished using a microscope with a travelling stage and eyepiece graticule or with an automatic particle counter. The size of the particles is determined by separating them according to size during sampling or by separating out the different sizes of collected particulate in the laboratory, using a microscope (Walton, 1954)¹ or liquid settling (Drinker and Hatch, 1954).²

When a particle is released from rest and falls in air, it is subject to the downward force of gravity and the opposing aerodynamic drag of the atmosphere. Balance between these forces is readily attained and the particle falls with a steady velocity known as its terminal velocity. Over a wide range of sizes, from approximately 1 to 50 microns, the terminal velocity is proportional to the specific gravity of the particle, ρ , and the square of its diameter, d . When the diameter is expressed in microns, the terminal velocity of a spherical particle falling freely in air is approximately $0.003 \rho d^2$ cm/sec or $0.006 \rho d^2$ ft/min. The terminal velocity of particles is dependent on the aerodynamic properties which also determine the proportion of inhaled particulate that deposits in the respiratory tract and the site of deposition (Lippmann, 1970).³

The preferred 'diameter' or size of a particle is its 'equivalent', or 'aerodynamic' diameter. This is equal to the diameter of spherical particles of unit density which have the same falling velocity in air as the particle in question. For some types of particles with extreme shape, other parameters are sometimes used. Thus, asbestos fibers, which are very long in relation to their diameter, are characterized by their length.

Amongst particles which are inhaled, those with an equivalent diameter greater than 20 microns are deposited by impingement in the nose and upper respiratory tract. Smaller ones down to 0.5 micron in diameter are carried into the smaller airways and alveoli, and are deposited there under gravity.

Those between 0.1 and 0.5 micron in diameter are also inhaled, but are mostly exhaled with the air since their terminal velocity is so low that there is not sufficient time for them to be deposited in the time the air is in the respiratory tract. The very smallest, those whose diameter is less than 0.1 micron, have such a small volume and mass that they have significant Brownian motion from the irregular impact of gas molecules, and are deposited readily. However, their weight is so small that particles smaller than 0.1 micron dia-

meter seldom make up a hygienically significant proportion of the inhaled particulate. The above diameters refer to the size of the separate airborne entities, each of which may consist of several particles clumped together. It is the aerodynamic properties of these clumps rather than those of the individual particles which determine where they will be deposited.

THE PURPOSE OF SAMPLING

The main reason for sampling for atmospheric particulates is to estimate the concentration in the air which is inhaled by the employees. A determination may be made of the concentration of all the particles or just those which have particular sizes or shapes. This is done in order to assess whether there is a risk to the health of workers exposed to the environment. This judgment is made by comparing the results against hygiene standards.

The results obtained by atmospheric sampling depend very much on the time and place where the samples are taken and the type of instrument used. Those concerned with setting hygiene standards usually take account of the wide variation in the results that may be obtained, and take great care that there shall be no misinterpretation of the values inserted in the standards.

Variations in Time

Dust concentrations can vary around the average value from zero up to 2½ times the average, even in conditions where the work appears to be done at a steady rate. The appropriate hygiene standard may place an upper limit on the average concentration over a work shift, or on the maximum concentration during this period, or both.

Variations in Space

It is important to determine the concentration in air which may be inhaled. When planning and executing a survey of the particulates in workroom air, one should bear in mind that the concentration close to a machine or process is usually quite different from the concentration in the inhaled air. As a general rule, the concentration may vary considerably over a distance of a few feet, or even over a distance of a few inches. This is especially true when there are few sources of contaminant and the employees work close to a source. There should be no physical obstruction between the air sampler inlet and the operative's nose and mouth. Whenever there is any doubt, the sampler inlet should be within a foot of the operative's nose and mouth, and yet be out of the line of sight.

Variations between Instruments

Unfortunately, no two different types of airborne particulate sampler yield the same result. It takes the most painstaking tests to yield similar results from two identical instruments. Therefore, the instrument used must be the same type and must be used in the same way as that inferred in the hygiene standard. Thus, when using the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs) of airborne contaminants as hygiene standards (Threshold Limits Committee, ACGIH, annually) the documentation on particular sub-

stances must be consulted to verify the methods to be used. (Threshold Limits Committee, 1971).⁴ As a general rule the substances in the main list of values should be collected with total dust sampling instruments and the weight concentration should be determined. Those listed under "Mineral Dusts" should be collected according to type, either with an impinger, total dust sampler, respirable dust sampler, or membrane filter. It is inadvisable to rely upon converting the results from one type of sampling instrument or method into those which might be obtained from another sampling instrument or method.

THE VOLUME OF THE SAMPLE OF AIR

People at work inhale about 10 cubic meters of air in 8 hours, depending on their energy expenditure. Those who work physically hard may inhale 20 cubic meters and those with sedentary occupations only 5 cubic meters. However, the volume of the sample of air taken for assessment of particulate concentration need not equal, or even be related to the volume of air inhaled. The primary need is to obtain a representative sample of the air of sufficient volume to contain enough particles that can be accurately weighed, counted or chemically analyzed. The volume of the sample of air may be as little as 5 ml or more than 50 cubic meters. The whole sample or a small fraction of it, perhaps 1 percent or less, may be assessed. The concentration of particulates in atmosphere which may be safely inhaled is very low, so a high flowrate is generally desired to collect the required quantity of particulate in a short time. The sampling gear should also be sufficiently portable to enable sampling at the place of work, as near to the operative's nose and mouth as practicable. Particulate sampling instruments which have the highest flowrates tend to be the least portable. Some portability may also be sacrificed so as to collect a large quantity of particulate and thereby to simplify the laboratory assessment.

The limit to the sensitivity of a given weighing procedure or analytical technique effectively sets a minimum to the required volume of air which constitutes a sample. The sampling procedure and method of assessment should be sensitive enough to measure the concentration in air of one-tenth the hygiene standard. Therefore, the minimum volume of the sample of air must be

$$\frac{10 \times \text{analytical sensitivity}}{\text{hygiene standard concentration}}$$

When the analytical sensitivity is measured in milligrams and the hygiene standard in milligrams per cubic meter, the volume of the sample of air is given in cubic meters.

THE DURATION OF EACH SAMPLE PERIOD

The minimum duration of the run for each sample depends upon the volume flowrate of the sampler.

$$\text{Minimum duration per sample} = \frac{10 \times \text{analytical sensitivity}}{\text{Hygiene standard concentration} \times \text{flowrate}}$$

Units should, of course, be consistent in the above formula.

The sensitivity of different weighing or analytical procedures can be very different. Therefore, the analytical sensitivity must be known in order to proceed with the sampling in an orderly and effective manner. For example, a common element in many particulate sampling procedures is a cellulose filter paper which is weighed before and after sampling. The filter paper may weigh anything from 0.05g to 5g according to size. The sensitivity of the weighing procedure is limited by difficulties arising from the equilibrium water content of the cellulose in moist air, which varies with humidity and temperature. When the filter papers are dried to constant weight or comparison unused filters are used as a 'tare', cellulose papers may be weighed to 0.1 percent of the weight of the paper. Thus,

$$\text{Minimum duration of sampling} = \frac{0.01 \times \text{weight of paper}}{\text{Hygiene standard concentration} \times \text{flowrate}}$$

Where the duration of the sampling is expressed in minutes, the hygiene standard is in mg/M³, the flowrate is in liters per minute and the weight of the paper is in milligrams:

$$\text{Minimum duration of sampling (mins)} = \frac{10 \times \text{weight of paper (mg)}}{\text{TLV (mg/M}^3) \times \text{flowrate (l/min)}}$$

Another useful form of the same equation is given by calculating the volume of air to be sampled. Thus,

$$\frac{\text{TLV (mg/M}^3)}{10} = \frac{\text{wt. of paper (mg)}}{\text{vol. of sample (l)}}$$

Similar expressions can be found for other weighing or analytical procedures and as such are extremely useful for choosing a satisfactory combination of sampling method, duration of sampling and flowrate.

INSTRUMENTATION

Sampling Trains

A sampling train for particulates has the following critical elements in this order: air inlet orifice, particulate separator, air flowmeter, flowrate control valve and suction pump. Equally important are the motor and power supply for the pump and the power supply, if any, for the particulate separator.

The Air Inlet. The air entry orifice should be as short as possible to keep wall losses to a minimum. Nevertheless, it is sometimes necessary to have a probe tube connected to the air inlet as in the case when the concentration of particulate is highly localized. Having the entry at a floor- or bench-mounted instrument might result in a false reading. Wall losses may be excessive in probe tubes which are longer than three feet or have sharp bends. In such cases the particulate in the tube must be dissolved or washed off and added to the sample. If the particulate separator is small and light, a length of tubing may be inserted between it and the air flowmeter to avoid the problem of wall losses in a probe tube upstream of the separator.

The Particulate Separator. The particulate separator is the most important element in the sampling train. The efficiency must be high and reliable. The pressure drop across the separator should be low in order to keep to a minimum the size of the necessary suction pump and motor. It may consist of a single element such as a filter or impinger or there may be two or more elements in series, so as to separate the different sizes of particles.

The Air Flowmeter. The air flowmeter is commonly an air rotameter, but may be a gas-meter or an orifice meter.

Where the flowrate is constant or automatically controlled, there may be only an on-off indicator that the device is functioning. In such cases the flowrate through the sampling train is measured in the laboratory and checked after sampling. The flowrate should be checked with the sample of particulate in place since sometimes the filters affect the flowrate drastically.

Similar considerations apply in sampling trains with an integral flowmeter. The value shown by a rotameter, gas-meter or orifice meter is partly dependent upon the air pressure at the entry to the meter, and upon the magnitude and frequency of pulsations in the air flow. Measurement of the air flowrate, or calibration of the flowmeter should be performed before and after sampling, with all the elements of the sampling train in circuit.

Flow Control

The flowrate control may be manually operated if in the form of a needle valve or a simple pinch valve. When filters are employed the flowrate control may need repeated adjustment while sampling, since particulates clog the filter. This effect may be mitigated by using a sampling train with a high internal resistance. Automatic flowrate control may be obtained with a critical orifice. Otherwise, electrical or pneumatic means may be utilized.

A critical orifice is a simple and popular means of achieving constant flow. The principle of the method is to draw the air through the orifice under "critical" flow conditions and constant upstream pressure.

The volume flowrate of a gas into an orifice increases as the pressure differential across it increases until a point is reached when the air is moving through the orifice at a velocity equal to the velocity of sound through the gas. The volume flowrate then stays the same for any further increase in pressure differential. The downstream to upstream pressure ratio below which the volume flowrate becomes constant is known as the critical pressure ratio. This is approximately 0.53 for air through a well-rounded orifice. At atmospheric pressure upstream, the flow becomes critical as the downstream pressure is reduced below 400 mm mercury. The orifice is placed in the sampling train at the entry or at a point where the upstream pressure is constant, and the pressure differential is maintained in excess of 400 mm mercury. The critical pressure drop, 400 mm mercury, reflects a resistance to flow. This may be reduced by making a gradual enlargement or easé on the discharge side of the orifice in the

form of a 1-in-5 enlargement for 15 orifice diameters. This reduces the necessary overall pressure drop because of the pressure recovery in the expansion piece. In practice, an orifice having an overall pressure drop of 100 mm mercury at critical flow is made fairly easily.

A critical orifice should be calibrated from time to time as it may become worn by the particulates passing through it.

If a critical orifice is not used the flowrate may be maintained constant with devices downstream of the particulate separator, such as by having a flow-regulating valve followed by a pressure-regulating valve downstream. The pressure drop necessary to maintain control with this latter system is about 250 mm mercury.

Even with particulate separators which have a resistance independent of the dust loading, it is advisable to have a pressure-regulator as the performance of most pumps tends to vary with time.

The Pump

The suction pump is commonly a motor driven rotary pump but other kinds are also used, including diaphragm pumps, centrifugal fans, hand operated crank pumps or piston pumps. The pump must produce sufficient air horse-power and draw the necessary flowrate through the sampling train under the most adverse conditions of air-flow resistance. When making up a sampling train, it is helpful to measure the air-flow resistance contributed by each element, as it is often found that a high resistance contributed by a secondary element such as tubing, elbows, connections or other fittings can be easily reduced. The weight of the necessary pump and motor increases roughly in proportion to the pressure drop and the flowrate through the system. Rotary pumps utilized in this work to produce a fairly high pressure drop of 50-350 mm of mercury are generally the sliding vane type although multi-lobe blowers or gear pumps can be used. Centrifugal fans are suitable where the pressure drop through the sampling train is less than 10 mm of mercury. Somewhat higher pressure drops, up to 100 mm of mercury, can be sustained with small multi-stage centrifugal turbines. If the required sample volume flowrate is less than 5 liters per minute, diaphragm pumps and piston pumps can be used. The very lowest flowrates, less than 100 cc per minute, are accommodated by water displacement apparatus.

Power Supply

The power supply is commonly line current, but nickel-cadmium rechargeable batteries may be used on the smaller sampling trains and are essential for the greatest portability. Otherwise, manual operation is used. Disposable dry cells are not very suitable but they have been used. Sometimes electricity is not available on site or is banned for reasons of safety, so hand power or approved coal mine dust personal sampler pumps may have to be used, or compressed air or water ejectors may be feasible. Compressed air ejectors can provide flowrates up to 200 liters/minute against 400 mm of mercury pressure drop, utilizing compressed air at a pressure of 20 lbs. per square inch. Low sampling flowrates, up to

10 liters per minute, may also be obtained with small ejectors working from bottled Freon, carbon dioxide or compressed air.

COLLECTION DEVICES

Particulate Separators

Usually particulate separators are suitable for determining either the mass concentration or the number concentration. Nowadays, the mass concentration instruments are divided into two broad categories, those with and those without a pre-selector.

The pre-selector separates those particles which are larger than about 5 microns. (Task Group on Lung Dynamics, 1966).⁵

Filtration

Many instruments used in assessing the mass concentration of airborne particulates incorporate a filter. Common filter paper consists of an irregular mesh of fibers about 20 microns in diameter or less. Air passing through the filter changes direction around the fibers and the particles in suspension impinge there.

The largest particles, those greater than about 30 microns, also deposit to a significant extent by direct interception or by sieving action, and the very finest particles, less than 0.5 micron, also deposit through their diffusion caused by Brownian motion. With particles greater than 0.5 micron diameter deposition efficiency generally increases with the velocity of the airstream and with the density and diameter of the particles. Deposition by diffusion dominates over deposition by impingement of the very smallest particle sizes and decreases as the diameter of the particles increases. Consequently, there is a size at which the combined efficiency by impingement and diffusion is a minimum. This is always below 0.5 micron diameter and usually below 0.2 micron diameter.

The weight of particles below 0.5, and certainly of those below 0.2, micron diameter, is usually less than 2% of the airborne dust of hygienic significance so that in practice the amount of deposition by diffusion may be ignored. Samples which consist primarily of freshly formed metal fumes would be exceptions.

Cellulose fiber filter papers are relatively inexpensive, are obtainable in an almost unlimited range of sizes, have high tensile strength, show little tendency to fray during handling and are low in ash content. Their main disadvantage is their hygroscopicity, which must be allowed for in the weighing procedure. Whatman No. 41 is the most widely used cellulose filter as it combines good efficiency with low flow resistance.

Filters made of glass, asbestos, ceramic, carbon or polystyrene fibers less than 20 microns in diameter have a higher efficiency than cellulose filters and may be favored for this reason. However, their principal advantage over cellulose filters is the ease of determining the blank weight, and this is the reason that glass fiber papers have become very popular in recent years. The resistance of a filter increases with thickness and compression of the filter mat and with the dust loading.

A good filter material for particulate sampling

is made of thickly matted fine fibers and is small in mass per unit face area.

Membrane Filters

Membrane filters may be used to collect samples of particulates for examination under the microscope. They are thus used to determine number concentration as well as mass concentration.

A membrane filter is a micro-porous plastic film made by precipitation of a resin under controlled conditions. The polymers used are cellulose esters, polyvinyl chloride or acrylonitrile. These filters are not very stiff and are therefore supported on a metal gauze or other grid. Special types have an integral nylon support to give added strength. In manufacture the pore size is controlled within close limits, and membrane filters are obtainable with mean pore sizes of from 0.01 micron to 10 microns in diameter. They are usually 140 microns thick, and have an efficiency close to 100% for particles larger than the mean pore size. On the surface, the particles are filtered out in a sieving action so they may be examined under the microscope as on a glass slide although many particles smaller than the nominal pore size are trapped within the filter. They are obtainable with a grid stamped on, which facilitates counting over a known area. They may also be obtained black, which is advantageous for certain white, opaque dusts. Common types are soluble in cyclohexane or other organic solvents, which facilitates separation of the particulates when required.

When immersion oil is placed on a membrane filter, it becomes transparent and the particles may be examined under the microscope by transmitted light. Difficulties arise with minerals whose refractive index is close to that of the filter material.

Membrane filters may be used in the determination of mass concentration where it is feasible to employ a low air sampling flowrate. They have a high air-flow resistance. A common membrane filter used for dust sampling has a nominal pore size of 5 microns.

Impingement on a flat plate

Some particulate separators rely upon impingement on a flat plate held close to a jet of the air containing the particles in suspension. These have been used for many years. Their popularity is waning but they still are an important type. These instruments are operated by drawing air at very high velocity, 50-300 meters per second, through a small jet. The jet may be circular or rectangular in cross-section, 0.5 mm to 1.0 mm in diameter or width, and 1 mm to 5 mm from the deposition surface. Particles down to about 1 micron diameter are efficiently thrown out by the centrifugal force as the air in the jet turns through 90 degrees or more.

The forces involved are not sufficient to remove particles much smaller than 1 micron in diameter. With high velocity jets the coarser particles are thrown with increasing force against the plate and may bounce off, or break up. The surface of the deposition plate is usually wetted or greased to cushion the particles and trap them.

The collected particles are counted by eye under a microscope and the result is a useful comparative index of the concentration of particulates in the sampled air. The count obtained in a particular concentration is very dependent on the specific type of instrument and the nature of the particulate so that the counts obtained with other types may be different by a factor of up to 10. Therefore, it is imperative to use the same type of impingement instrument when making repeat surveys in a given environment.

Electrostatic Precipitation

Electrostatic precipitation has been utilized successfully in atmospheric sampling. These systems have the advantages of negligible flow resistance, no clogging and precipitation of the dust on a metal cylinder whose weight is unaffected by humidity. A power pack is needed to supply the high voltage and precautions have to be taken to guard against electric shock.

The wire and tube or "tulip" system is used. The tube is a light alloy cylinder about 6 in. long and 1½ in. dia., held horizontally. The tube is grounded.

A stiff wire, supported at one end, is aligned along the center of the tube and serves as the charged electrode. The tip of the wire is sharpened to a point. A high d.c. voltage, between 10 kv, and 20 kv, is applied to this central electrode. The corona discharge from the tip charges the particles in suspension in air drawn into the tube. Under the action of the potential gradient between the wire and the tube the charged particles migrate to the inside surface of the tube.

The migration velocity of the charged particles greater than 1 micron in diameter increases in proportion to particle diameter. On the other hand, migration velocity is approximately independent of particle diameter for particles smaller than 1 micron in diameter. Therefore, very high separation efficiencies are attainable with electrostatic precipitators and they are ideal for particles smaller than 1 micron in diameter.

Thermal Precipitation

A particle in a thermal gradient in air is subject to differential molecular bombardment from the gas molecules, so that it is subject to a force directed away from the hot sources. This is the principal mechanism involved in thermal precipitation. The air is drawn past a hot wire or plate and the dust collects on a cold glass or metal surface opposite the hot element. A high thermal gradient is needed so the gap between the wire or plate and the deposition surface is kept small (0.5-2 mm). The migration velocity induced by the thermal gradient is small, and very nearly independent of particle diameter. However, the system has severe limitations in the maximum flowrate possible with high deposition efficiency. It is, therefore, used only for collecting sufficient particulate for examination under the microscope. Due to the temperature involved it is not suitable for mists except those of liquids with high boiling point.

When the particulate is collected on a glass coverslip and viewed dry, the visibility of the

particles under the orthodox light microscope is far better than that obtained with a membrane filter.

Elutriators

Elutriators are an important and sometimes essential feature of sampling trains used for mineral dusts. They are used as pre-selectors, ahead of other particulate separators to remove the larger particles. There are two classes of elutriators employed in sampling air for particulates: horizontal elutriators and vertical elutriators.

A single element of a horizontal elutriator used in this work is a thin, horizontal, rectangular duct. Commonly the horizontal elutriator package consists of several such elements stacked one above the other, connected in parallel to a common exit. (Walton, 1954).⁶ The theory is fairly easily understood and performance closely matches theory. Suppose a flowrate, Q , of air is passing uniformly along a horizontal duct of length L , width W and height H . The time, T , it takes for air to pass through the duct is LWH/Q . Among the particles entering the duct those which, in time T , would fall freely under gravity a distance greater than H would all deposit on the floor of the duct. Thus, the minimum terminal velocity (V_c) for 100% capture by the elutriators, is

$$V_c = H/T = Q/LW.$$

Also, among those particles with terminal velocity, V , (V less than V_c) a proportion would be captured by deposition on the floor of the duct. The percentage captured in this way is $100(V/V_c)\%$. The proportion, P , not captured by the elutriator would be $100(1-V/V_c)\%$ of those with terminal velocity less than V_c .

$$P = 100 (1-V/V_c)\% = 100 (1-VLW/Q)\% \quad (1)$$

Thus, P is independent of the height of the duct, provided the floor area and flowrate are constant. It may also be shown that under streamline flow conditions, errors in the above formulae through assuming uniform flow cancel out. Flow is maintained streamline by making H small. Since the performance is independent of its height, the duct may be made as thin as practicable. All ducts with the same ratio of floor area to flowrate (LW/Q) have the same performance under streamline flow conditions.

A vertical elutriator is a single vertical tube, either parallel sided or in the shape of an inverted, truncated cone. The air with particles in suspension is drawn or blown upwards through the tube. Suppose a flowrate, Q , of air is passing uniformly up a parallel sided, vertical duct, cross-sectional area A . The upward air velocity is Q/A , equal to V_c . None of the particles which have a terminal velocity in air exceeding V_c , would be carried up the tube by the air. The particles with zero terminal velocity in air would be carried up the tube with velocity V_c . Those with a terminal velocity, V , between zero and V_c , would be carried up at a velocity $V_c - V$ and proportionately fewer would pass through the tube. The percentage, P , passing through the tube,

$$P = 100 (1-V/V_c)\% = 100 (1-VA/Q)\% \quad (2)$$

P is independent of the length of the tube, pro-

vided the cross-sectional area and flowrate are constant. It is important to maintain streamline flow in elutriators so their cross-sectional area must be small. However, since the performance of a vertical elutriator is dependent on cross-sectional area, this type is only used in sampling at very low flowrates.

The conical form of vertical elutriator, with a small entry at the tip at the bottom, is used to promote smooth flow through the elutriator. A parallel portion is usually arranged at the top, where the cross-sectional area is largest and the final performance therefore determined.

Perfect streamline flow is not realized in practice even with horizontal elutriators. The effects of a disturbance to streamline flow on the collection characteristics may be understood by considering the collection characteristics of a horizontal elutriator under conditions of perfect mixing. At a point a distance l from the entrance to an elutriator element of width W , length L and height H the average forward velocity of the airstream,

$$\frac{dl}{dt} = \frac{Q}{WH}$$

The horizontal base area of small element length $d1$ is $Wd1$. The number of particles of terminal velocity V falling on this area in time dt is thus

$CVW d1$ particles per minute, where C is the concentration of particles in the air over the element.

The volume of the air above the element is $WH d1$, thus the rate of change of concentration with time,

$$\begin{aligned} \frac{dC}{dt} &= \frac{-CVWd1}{WHd1} \\ &= \frac{-CV}{H} \end{aligned}$$

From which

$$C = C_0 \exp - (Vt/H),$$

where C_0 is the concentration at t_0 , when the air enters the elutriator. The time to pass through the elutriator is LWH/Q , so that the concentration at

the exit is $C_0 \exp - (VLW/Q)$. Thus the percentage, P , of particles in the air entering the elutriator which pass through it without depositing,

$$P = 100 \exp - (VLW/Q) \quad (3)$$

Elutriators are commonly designed on the assumption of uniform flow, and so as to capture 50% of particles of 5 microns equivalent diameter. (Orenstein, 1960).⁷ The expected performance of such an elutriator under streamline flow (equations 1 and 2) and under perfect mixing conditions (equation 3) are shown in Fig. 13-1.

Streamline flow is often nearly achieved and the performance comes close to theoretical. (Hamilton, 1967).⁸ Such elutriators have an inherent fail-safe feature in that if due to distortion of the plates or poor design streamline flow is seriously disturbed, capture of coarse particles is reduced and the estimated sample concentration errs on the high side. On the other hand, flowrate control is

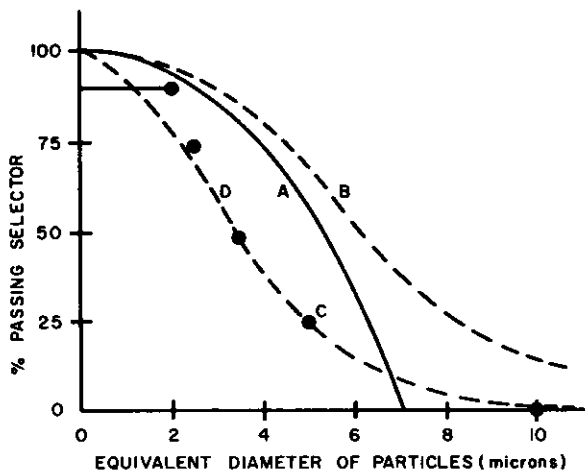


Figure 13-1. The Performance of Horizontal Elutriators Line A - Streamline flow conditions; elutriator designed to allow 50% of particles of 5 microns equivalent diameter to pass through — Line B - Perfect mixing in elutriator designed as for Line A — Points C - Size selector characteristics recommended by the ACGIH for “respirable” dust sampling — Line D - Perfect mixing conditions; elutriator designed to allow 50% of particles of 3.5 microns equivalent diameter to pass through.

particularly important. If the flowrate is low, coarse particles are removed to a greater extent, giving an additional error on the low side. The reverse occurs when the flowrate is high.

Cyclones

Miniature cyclones of simple construction have been used in recent years as pre-selectors ahead of other particulate separators, and serve the same purpose as elutriators. Cyclones 10 mm to 50 mm diameter are employed, for example, when testing compliance with current Threshold Limit Values for “free” silica; that is, quartz, cristobalite, tridymite and fused silica dust (Threshold Limits Committee, 1972).⁹

The air enters a cyclone tangentially at the side of a cylindrical or inverted cone shaped body, swirls around inside and leaves along the axis from a tube at the top. Coarse dust is thrown to the side and collects in the base of the cyclone. The air velocities in a cyclone are very high and the flow is highly turbulent.

The centrifugal acceleration of a particle in the rotating airstream turning at an angular velocity, ω , is $\omega^2 r$, where r is the radius of rotation. The diameter of cyclones in common use and the flowrates employed give centrifugal accelerations in excess of one hundred times gravitational acceleration. The air in a cyclone rotates several times before leaving and consequently the dust deposits as it would in a horizontal elutriator of floor area several times the cyclone outer surface area, and under a force over one hundred times gravity. Consequently, the volume of a cyclone is

much smaller than a horizontal elutriator with the same flowrate and efficiency.

The characteristics of a size selector for testing compliance with current Threshold Limit Values for free silica are indicated in Fig. 13-1, at points C, and the size-efficiency performance of an elutriator under perfect mixing conditions to simulate this are indicated in Fig. 13-1 at line D.

Cyclones have similarly shaped size-efficiency performance curve. However, the detailed pattern of air-flow through a cyclone depends so much on the design adopted that the performance of cyclones of particular design must be checked experimentally.

The orientation of a cyclone is not as critical as that of an elutriator so a small one may safely be fastened to an operative’s clothing. Further, small errors in flowrate are counter-balanced to some extent by changes in the size-efficiency characteristics. Thus, if flowrate is low, coarse particles are removed to a lesser extent, giving an opposite error, and the reverse occurs when the flowrate is high.

The air-flow resistance of a cyclone is higher than that of an elutriator for the same flowrate. Nevertheless, the resistance is largely independent of dust loading and small in comparison with the resistance of customary filters downstream.

CHOICE OF SAMPLING INSTRUMENTS

There are at least 50 different types of sampling instruments used in particulate sampling, each with its own proponents. Further, there are new ones being developed every month. Amongst those in regular use at the present time for determining concentration as mass of particulate per unit volume of air are the electrostatic precipitator and many filter paper methods. The common instruments for determining the concentration as number of particles per unit volume of air are: the impinger, the membrane filter method, the thermal precipitator and the light scattering automatic particle counter. All these instruments and many others are described in “Air Sampling Instruments.” (American Conference of Governmental Industrial Hygienists, 1972).¹⁰

The choice of instrument in particular circumstances is very often dictated by the limited choice of instruments actually in the hands of the hygienist at the time the measurements are needed. The problem may be one of deciding which of two not very suitable instruments is least likely to give rise to erroneous conclusions rather than one of choosing the ideal instrument. For example, when sampling for a mineral dust, a “respirable” dust sampler may be needed. However, the sampling equipment available for total dust measurements is simpler and less expensive than that for respirable dust. If the proportion of fine dust in all the airborne dust is known, the concentration of fine dust in the air could then be inferred from a simple measurement of the concentration of all the atmospheric dust (total dust).

In particular cases, upper limits can be placed

on the proportion of fine dust, recognizing that in effect an additional factor of safety is thereby incorporated. Again, in the absence of any precise information on the proportion of fine dust, the total dust concentration may be used as a working limit. Obviously, if the total dust concentration is less than a certain value, any fraction of it will also be less than this same value.

Thus, lack of elutriators, cyclones or other pre-selectors need not necessarily be a bar to proceeding with mineral dust sampling in an orderly and effective manner. In many cases the simplest of measurements will suffice. In others, the proportion of fine dust is so small that a more sensitive and precise method incorporating a pre-selector is justified.

Similarly, in addition to the particulate being studied, background material and other contaminants are also collected. It is necessary to consider whether simply to weigh all the particulate, recognizing the safety factor that would be incorporated by assuming it was uncontaminated, or to analyze the particulate in the laboratory. The procedure selected influences the choice of sampling instruments as each procedure possesses a different sensitivity. Taking an example from number count instruments, when determining an airborne asbestos dust exposure, it has to be borne in mind that the thermal precipitator, impinger and Royco particle count are progressively simpler techniques from the operational standpoint, but less easily related to the membrane filter fiber count needed for asbestos dust.

Electrostatic Precipitators

Electrostatic precipitators normally do not have a preselector ahead of the collecting tube. They are therefore suitable for all those particulates listed in the TLV document of the ACGIH except mineral dusts evaluated by count. They may also be used for nuisance particulates. Because of the high efficiency for separating particles smaller than 1 micron in diameter, they are very often used when sampling for fumes. The two types commercially available are the Mine Safety Appliances Electrostatic Sampler and the Bendix Electrostatic Air Sampling System. The former has a fixed flowrate of 66 l/min from a 50 c/sec frequency supply, and the latter is variable between 90 l/min and 200 l/min. The ionizing voltage should be maintained sufficiently high to collect all the particles but not so high as to produce arcing between the central electrode and the collecting tube. A check that the dust has all been collected is to observe that the downstream end of the collecting tube is clear of dust. There is a practical limit of about 100 mg to the amount of dust that can be collected on each tube, as a thick layer of dust is easily dislodged and may be lost on handling. For very high dust concentrations, a coiled filter paper liner may be used to enable higher dust loads to be carried successfully. The ends of the sampling tube should be capped when the sample has been collected and the outside of the tube wiped clean. The dust may be washed or wiped off the tube. If the tube is washed, it

should be allowed to return to room temperature before weighing, or balance errors will occur. The tube can be weighed on a semi-micro balance to 0.25 mg.

Filter Methods

So-called 'respirable' dust sampling instruments include a pre-selector to separate the coarser particles before collection. (Aerosol Technology Committee, 1970).¹¹ These instruments normally incorporate filters to collect the fine particulate. Such instruments without a pre-selector are suitable for other particulates in the ACGIH list of TLVs.

The Casella Gravimetric Dust Sampler Type 113A incorporates a horizontal elutriator for a flowrate of 2.5 l/min (Dunmore, Hamilton and Smith, 1964)¹² and the Casella Hexhlet incorporates a horizontal elutriator for a flowrate of 50 l/min (Wright, 1954).¹³ In both instruments the fine dust is collected on a filter.

In the Dorr-Oliver and Mine Safety Appliances respirable dust samplers the size selection is achieved by using a small cyclone upstream of a filter. Where a 10-mm nylon cyclone is used, the flowrate is 1.7 l/min and for the UNICO ½-inch HASL cyclone, 9 l/min.

With all respirable dust samples, it is particularly important to maintain a constant and non-pulsating sampling flowrate to ensure correct size selection characteristics.

A particulate sampler without a pre-selector and incorporating a filter may be made up from parts available in the laboratory. Whatman No. 41 cellulose filter paper or GF/A glass filter paper are used.

The principal source of error in weighing cellulose papers arises from the hygroscopic nature of the paper. This error can be kept within bounds by strict observance to a drying and weighing routine. The flowrate, sampling interval and size of filter are then chosen to yield a weight of dust amounting to at least one percent of the paper, and preferably more than two percent.

Glass fiber filters are available either with or without an organic binder. The binder increases the mechanical strength of the paper. Glass fiber filters without binder are used when the binder would constitute an interference in the analysis for organic matter in the particulate. Even with the binder, glass fiber filters are quite friable and must be handled with care. Analysis of the dust for iron, aluminum, sodium, potassium, magnesium and silica is not possible because of interference from large amounts of these in the glass fibers.

Polystyrene fiber filters such as the Microsorban filter, have a flow resistance which is relatively low, being comparable to Whatman No. 41, while their efficiency of collection is relatively high and is comparable to that of glass filters. Since they have poor mechanical strength, they must be well supported in the filter holder.

Membrane filters have a low mass and low ash content. However, they have a high flow resistance. Cellulose filter paper such as Whatman

No. 41 has an air flow resistance of 10 in. water gauge when the face velocity through the paper is 50 cm per sec, whereas a membrane filter with a pore size of 2 microns or less has an air flow resistance of at least 50 in. water gauge under the same conditions. Particle collection takes place almost exclusively at the surface of the filter, and when more than a single layer of dust particles is collected on the surface, the resistance rapidly increases and there is a tendency for the deposit to slough off the paper.

A filter holder should be used which provides a positive seal at the edge, without leakage. It must not abrade or tear the filter. A screen or other mechanical support may be required for the filter, to prevent rupture or displacement in service. A back-up screen is necessary with glass fiber, polystyrene and membrane filters.

Filter thimbles are available in cellulose fiber and cloth. They are sometimes filled with loose cotton wool to reduce clogging. The advantage of a filter thimble is that large samples can be collected before clogging.

A typical procedure for weighing filters is as follows:

The weighing vessels used in a typical procedure are light screw-top cans with a pin-hole in the lid.

1. Remove the lid from a weighing vessel, place the filter inside and place the weighing vessel in a drying oven at 110°C. (60°C for membrane filters). Dry for 2 hrs exactly.
2. Screw on the lid of the weighing vessel and cool it in a desiccator with silica gel for exactly 20 min.
3. Weigh immediately.
4. Repeat steps 1 to 3. The two weights should check to 0.1 percent. Otherwise repeat procedure.

For most chemical analyses, it is necessary either to remove the sample from the filter, or to destroy the filter. Inorganic particles are usually recovered from cellulose paper filters by wet ashing (digesting in concentrated acid) or dry ashing (muffling, incinerating) the filter. Samples can be recovered from polystyrene and membrane filters by dissolving the filter in a suitable solvent.

The background level on the filter of the material to be analyzed must be determined. Filters contain various elements as major, minor and trace constituents, and the filter medium of choice for analyzing particular elements must be one with little or no background level for the elements being analyzed.

Impinger

The impinger is the instrument used in the series of studies by the U.S. Public Health Service 1925-1940 in dusty trades on which the Threshold Limit Values of the American Conference of Governmental Industrial Hygienists for Mineral Dusts were largely based. It is still a common method for mineral dust sampling in the United States, although it is being superceded by dry filtration. The dust-laden atmosphere is drawn

through a glass jet, the end of which is set a fixed distance from the bottom of a flask. The jet is immersed in water or alcohol and the particles strike the bottom of the flask and become suspended in the liquid.

A sample of the liquid is then placed in a counting cell and the particles are counted using a low-power microscope. The sampling time is usually 10-30 min or more. When long sampling times are used, the suspension can be diluted to the point where coincidence errors are insignificant.

The following method represents standardized methodology for the impinger sampling technique:

The sampling instrument is the standard impinger, operated at a rate of 1.0 cfm \pm 5 percent at 3 in. mercury negative pressure, or the midget impinger operated at 0.1 cfm \pm 5 percent at 12 in. water negative pressure. The sampling instrument and the indicating gauge on the flow-producing apparatus should be calibrated at regular intervals.

Counting Cell

The counting cell should be no more than 1.0 mm and no less than 0.25 mm in depth with an allowable variation of \pm 5 percent from the nominal depth.

Optical System

- A. The microscope should be equipped with the following:

objective	10X (16 mm) 0.25 N.A.
ocular (eyepiece)	20X
condenser	0.25 N.A.

- B. The counting area is defined by an ocular grid such as a Whipple disc and should be accurately measured by means of a stage micrometer.

- C. Kohler illumination is used except that after this has been achieved, the eyepiece is removed and the iris diaphragm of the microscope condenser is closed until the disc of light seen in the back lens of the objective is about one-half of the lens. Further reduction of brightness may be accomplished, if desired, with neutral density filters.

Collecting Liquid

The collecting liquid usually is 95% ethyl alcohol although distilled water or mixtures of distilled water and alcohol (ethyl or isopropyl) may be used.

Treatment of Collected Samples

- A. All glass-ware must be clean and the equipment protected against dust contaminants in the field. One impinger flask, a "blank" flask, is treated exactly like the others except that no air is drawn through it.
- B. The diluting liquid should be 95% ethyl alcohol.
- C. The impinger nozzle is rinsed down inside and out with diluting liquid as the sample is made up to a known value. Samples

having a low concentration of dust are diluted as little as possible. Dense samples are diluted so that no more than about 2,000 particles/mm² will appear in the counting area of the cell. Not less than 5 ml of original or diluted sample should be taken for further dilution, and dilutions should be made in steps not exceeding 10 parts of dilution liquid to 1 part of original or diluted sample. The dust suspension must be shaken vigorously by hand for at least 30 sec. before a portion is removed for dilution.

Preparation for Counting

- A. The sample to be counted is shaken to ensure a uniform suspension and a portion is transferred immediately to a clean cell by means of a clean pipette, taking care to prevent the inclusion of air bubbles.
- B. Two cells are filled from each sample and from a "blank" flask.
- C. Sample counting should start at the end of the settling time and should be completed in 10 min. The settling time should be 30 min/mm of cell depth.

Counting

- A. Before counting, the ocular grid should be cleaned to remove dust particles.
- B. The counting plane is the bottom liquid-glass interface of the cell. The microscope is focused up and down slightly with the fine focus adjustment in order to bring individual particles in and out of focus for more positive detection and counting.
- C. Fields selected for counting should be uniformly distributed over the counting plane of the cell. Observation should not be made through the microscope while fields are being selected.
- D. At least five fields of equal area should be counted in each of two cells. For a dust sample, when the first five fields of the first cell counted yield a total count of less than 100 particles, additional fields of known area should be counted; the total area counted is recorded and used in calculation of concentration. For each cell from the "blank" flask only five fields need be counted.
- E. The same total area should be counted in the second cell as is counted in the first.
- F. Total counts from the two cells of the same sample should be compared; and when the ratio of the greater to the lesser count is larger than 1.2, additional pairs of cells should be counted until a pair yields counts which satisfy this criterion. The count of this pair should be used for calculating the concentration of the sample.
- G. Five fields of the same area as that used for dust sample counting should be counted in each of two cells from a "blank" flask. The average blank count should be used in calculation of net count. If the blank count exceeds 30 particles/mm² of counted area, all the samples should be rejected.

H. Observers are cautioned that their ability to see particles probably improves during the first few minutes of counting as their eyes become accustomed to the task. A brief period of counting is suggested prior to recording data. Fatigue can cause a deterioration in counting efficacy; conservative judgment should be exercised on when to discontinue counting because of fatigue.

Membrane Filters

The membrane filter method is commonly used for assessing asbestos dust exposure.

In order to view the dust under the microscope it is necessary to use immersion oil to render the filter transparent. The refractive index of membrane filters is about 1.5, close to that of chrysotile asbestos ($N_D = 1.55$), so that under ordinary illumination the chrysotile may itself be very nearly invisible when using an immersion oil closely matched to the filter. A phase contrast microscope is therefore used to increase the visibility of the chrysotile. The method given below is based on the standardized techniques recommended by the National Institute for Occupational Safety and Health.

Sampling Procedure

Samples for evaluation of asbestos exposure are collected on Millipore AA Membrane filters (37 mm diameter, 0.8 μ m pore size) by personal samplers operated by battery-powered pumps, worn by the employees. The filters are contained in plastic filter holders and are supported on thick pads which also aid in controlling the distribution of air through the filter. The face cap of the filter holder is removed and filter used open face during sampling. The sampling rate is about 2 liters/min. A minimum sampling period of 15 minutes (for evaluation of excursion limit) and several samples of up to 4 hours for evaluation of 8-hour average are normally required. Samples with a visible deposit may be too heavy to count; compare the appearance of the collected samples with a clean filter. Heavy concentrations of visible dust in the air (100 to 500 fibers/ml) may require short sampling periods of only 5 minutes, or less. The following specifications should be considered minimum for the microscope used for counting of asbestos fibers.

1. Microscope body with a binocular head and a fine focus accuracy of 0.005 mm.
2. Binocular with 10X Huygenian eyepieces
3. Porton reticle
4. Mechanical stage
5. Kohler illumination (preferably built in and having provisions for adjusting light intensity)
6. Abbe condenser with an adjustable iris
7. 40-45X (0.65-0.75 N.A.) Positive (bright field) phase-contrast objective
8. Annular ring condenser diaphragm (corresponding to the objective)
9. Phase ring centering telescope
10. Green filter
11. Stage micrometer

Counting

To prepare samples for microscopic examination, a drop of the mounting medium is placed on a freshly cleaned standard (25 mm x 75 mm) microscope slide, using a dropper or applicator.

Mounting the sample

The mounting medium used in this method is prepared by dissolving 0.1 g of membrane filter per ml of a 1:1 solution of dimethyl phthalate and diethyl oxalate. The exact proportions of the 3 components are not critical, but the medium must have as high a viscosity as possible without being difficult to handle. The index of refraction of the medium thus prepared is $N_D = 1.47$.

The volume of the drop is approximately 0.05 ml. A wedged piece about 1 cm x 2 cm is excised from the filter using a scalpel and forceps, and placed dust side up on the drop of mounting solution. A #1-1/2 coverslip carefully cleaned with lens tissue is placed over the filter wedge. Slight pressure on the coverslip achieves contact between it and the mounting medium. Clearing of the filter with this method is slow, requiring about 15 min. The sample may be examined as soon as the mount is transparent.

A minimum of twenty fields, located at random on the sample, or a sufficient number of fields to provide a minimum of 100 fibers, are counted and fibers having length greater than $5\mu\text{m}$ are recorded. Any particle having an aspect-ratio of 3 or greater is considered a fiber.

Royco Particle Count Method

In the Royco particle counter a thin filament of the particulate laden air is drawn past an intense light beam and the light scattered at right angles is sensed by a photo cell. Air is continuously drawn through the center of a hollow cube or chamber with windows in the sides. Particles in suspension scatter light from a tungsten filament lamp focused on the center of the chamber. The scattered light is viewed by a lens system and photomultiplier. The pulse train from the photomultiplier passes to a linear variable-gain amplifier and fixed-level discriminator and then to a decade counter.

Time switches automatically switch a sequence of size discrimination channels so that the count may be restricted to successive size ranges or to all particles above a lower size-limit. The standard model counts above 0.3 micron and in 14 stages up to 10 microns at 0.3-, 1-, or 3- or 10-minute intervals. The counts are read off, plotted on a pen recorder, or printed out. An optional filtered dilution system can be incorporated to reduce coincidence errors in high concentration.

Overall calibration is performed against monodisperse polystyrene latex spheres. The air is filtered through a membrane filter after passing the counting chamber so that the sample may be subsequently check-counted by eye, under the microscope.

The instrument is extremely expensive, large, complicated and not very portable. Its great advantage is that it is automatic and suitable for de-

termining the size distribution of mists. It must be noted that the accuracy of the Royco particle counter is dependent upon the surface characteristics, including shape, of the particles being counted.

Thermal Precipitators

Two types of thermal precipitators are at present in use, namely the "standard" thermal precipitator, manufactured by Casella, and the "long running thermal precipitator," designed and developed at the Mining Research Establishment, manufactured in clockwork pump form by Ottway and Casella, and in an all electric form by Casella.

In the standard thermal precipitator, dust-laden air is drawn vertically into the sampling head and down a narrow vertical channel between two circular glass coverslips. Halfway between these two coverslips is stretched a horizontal wire, heated electrically. Dust is deposited by the thermal effect, opposite the wire, in two strips on the coverslips.

At the sampling site, the instrument is assembled in the sampling position so that the air channel through the head is vertical. Current for the heating wire is supplied by a 6 V rechargeable battery. Alternatively, line power may be used with a transformer having a 6 V outlet in series with a rheostat and AC ammeter. Air is drawn through the sampling head at 5-7 cm^3/min .

In the laboratory the coverslips are mounted, dust side down, on microscope slides, and are viewed under the microscope.

The slide should first be examined under the 16-mm objective for any unevenness in density along its length, and any contamination of the cover-glass in areas remote from the deposit. The extent of the deposit should be clearly defined, and if, owing to heavy contamination, the edge of the deposit is not easily seen, the sample should be rejected.

The length of the deposit should be measured with a stage vernier under a 16-mm objective. A traverse should be selected either centrally or 2 mm from either end.

If the examination of the deposit under the 16-mm objective has shown that there is a defect where a traverse would normally be made, a new position should be chosen which is clear of defect, yet as near as possible to the original position.

The total length of the traverse counted should be 2 mm, 1 mm either side of the center of the dust deposit.

The projected areas of the particles are compared with the areas of the globes or circles on the eyepiece graticule. All particles whose sizes are greater than the 1-micron circle are usually counted. These may be either single particles or aggregates. The criteria for including an individual particle or aggregate in the count are as follows:

1. It falls within the specified size range.
2. At some stage in focusing, a clear margin

of separation is visible between the particle and all its neighbors.

The airborne dust is deposited over a very small area on the cover glasses and to avoid overcrowding, it is necessary to restrict the volume of air sampled. An endeavor should be made to obtain slides with an optimum of 50,000 particles larger than 1 micron with outside limits of 25,000-75,000. Slides with densities above and below these limits are liable to give a seriously inaccurate estimate of the dust concentration. The recommended method of illumination in the microscope is the Kohler system. A compensating 15 x or 17 x eye-piece is recommended with the achromatic type objective.

In the long running thermal precipitator (LRTP) the dust-laden air is drawn down a vertical passage, and along a horizontal channel, the floor of which is formed by a glass coverslip. Particles settle out from the air by gravity and the remainder are precipitated thermally beneath a heated wire. A sample of up to 8 hours duration can be obtained with this instrument, compared with 10-30 min for a sample using a standard instrument.

The instrument is hung or supported in the sampling position, with the top surface approximately horizontal. To reduce contamination, the sampling head may be sealed during the journey to and from the sampling position. The instrument should not be subjected to excessive bumping during the journey back to the laboratory and should remain in an upright position until the sample can be removed.

The counting procedure to be followed for LRTP samples is generally the same as described for standard thermal precipitator samples, the following being the main points of differences:

1. The slides should be set up on the microscope with the thermally precipitated zone to the left of the microscope stage.
2. The length of the traverse to be counted should be estimated by marking the position of the thermally precipitated zone under the 16-mm objective and then moving the microscope stage 1 mm to the left of this position and counting 14.5 mm to the right of this point — any particles outside these limits are to be regarded as contamination.
3. The traverse to be counted should be 6 mm from the most clearly defined end of the thermally precipitated zone.
4. The width of the deposit, to be used in calculating the result, should be measured at the thermally precipitated zone.
5. The dust deposits on these slides are occasionally heavy and the use of the full 60-micron graticule width may entail prolonged counts, producing fatigue and a falling-off in the counting accuracy. In such cases use may be made of the subdivision of the graticule to count either 40- or 20-micron traverses.

STATISTICAL CONSIDERATIONS

In order to determine how many samples to take, and where and when to take them, it is necessary to keep in mind the objective of the survey and to understand how to cope with the variations in the results that are obtained.

Begin by making a list of the people who are employed in a particular work-place or work-places. The place to sample follows from inquiry about where they are working. Surveys vary from "one time" to "continuous monitoring." In a one-time survey the objective is to find out as quickly as possible if the concentration exceeds the hygiene standard at the time the samples are being taken. Continuous monitoring refers to regular sampling over a period of weeks, months or even years to check whether the environment is deteriorating (or improving).

Representative Sampling

When several employees are doing similar jobs, the question arises which employees to investigate. For example, the sampling may be based on the reasoning that if the environment of those whose exposure is the greatest complies with the recommendations of the TLV document, then the environment of every employee in the group will comply. The hygienist should judge which employees are representative of those with the highest exposure. They may be those in the location where there is the most dust, or those who do their job in such a way as to produce the highest airborne dust concentration.

The alternative is to use a random sampling procedure through the whole group. Individuals from a group may be chosen by selecting names at random. They may be further subdivided into smaller groups exposed to markedly different dust concentrations, and each group sampled separately.

The spacing of samplings over the period under study should be planned ahead of time. The atmospheric samples may be taken at regular intervals or at times chosen at random beforehand. If taken at regular intervals the interval should not coincide with any other regular cycle of events which might be related to the concentration of atmospheric particulates.

Sampling by the Workday

Threshold Limit Values refer to the time-weighted average concentration for a 7- or 8-hour workday and 40-hour workweek. Samples of the atmosphere are often taken for periods of 5 to 30 minutes or for a full shift, depending on the apparent particulate concentration, the assessment procedure to be used, and the duration of the operation being studied. A 15-minute sample duration is used in many cases. The maximum number of such 15-minute results taken with one sampling instrument in an 8-hour workday is 32. Such a set of 32 results, whose average was lower than the TLV, could be taken as showing that the environment complied with the TLV document on that workday with respect to the airborne particulates being determined.

Particulate sampling procedures differ from this because often, for good practical reasons, only

a few results have been obtained, perhaps as few as four or five. When fewer than 32 15-minute results are obtained it is necessary that the acceptable upper limit of their average be made lower than the TLV to compensate for the loss of information.

The distribution of averages of two or more results is a normal distribution when the parent distribution is normal. More important, even if the parent distribution is not normal, the distribution of the average tends rapidly to normal form as the number of results increases. In most cases it may be assumed for all practical purposes that with four or more results their average is distributed normally. Consequently, the error of this average can, in practice, be estimated by reference to a table of the normal distribution. (Roach, Baier, Ayer and Harris, 1967).¹⁴ The standard deviation of the average of n results is σ/\sqrt{n} , where σ is the standard deviation representing the dispersion between the individual results.

Suppose, for example, the individual results obtained over the course of a shift varied about their average with a coefficient of variation of 35%. With 32 results, the 90% confidence limits of the average would be $\pm 10\%$ of the average. Thus, since only one side of the distribution is of concern, one would be at least 95% confident, when the observed average equals the TLV, that the true average did not exceed that TLV by more than 10%. If fewer than 32 results are available the same degree of confidence can be obtained only by lowering the acceptable upper limit of their average until the upper confidence limit again equals $1.1 \times$ TLV. In practice, the coefficient of variation may be less than, or vary much greater than, the example 35%. A general formula for the acceptable upper limit to the average, \bar{x} (max) given in terms of the standard deviation, σ , and the number of results, n , is:

$$\bar{x}(\text{max}) = \text{TLV} - 1.6 \left(\frac{1}{\sqrt{n}} - \frac{1}{\sqrt{32}} \right) \sigma.$$

When the standard deviation is not known from previous results, it has to be estimated from the sampling results. A simple and efficient estimate from a few samples is obtainable from the range. The possibility of error in this estimate is also taken into account by lowering the acceptable upper limit to the average accordingly. The limit so calculated may be found conveniently from Table 13-1.¹⁴ The limit is $\text{TLV} - (k \times \text{range})$, where k is found in the table, from the number of results obtained.

When the limit so calculated is less than the observed average, the environment cannot safely be said to have complied; and when the limit is higher than the observed average, it can be stated with some assurance that the environment did comply. In this way the hygienist can make a simple confidence test for compliance and make proper allowance for the number of sample results actually obtained.

Whereas it is possible to state that the conditions examined on a particular workday complied with the TLV document, it is not possible to infer from the results of sampling on one day

TABLE 13-1
k Values for the Range

Number of Results	k
32	0.
10-31	0.1
6-9	0.2
5	0.3
4	0.4
3	(0.8)
2	(0.9)

whether these conditions were representative of any other period.

The hygienist may choose the day to be sampled with the aim of sampling a day representative of the highest concentration. However, it must be borne in mind that, even with careful observation of the processes, cross-questioning of the employees, ventilation measurements, and studies of air contaminant control equipment, the judgment may be little more than intelligent guesswork.

The average concentration will vary not only from time to time during a day but also from one day to another, from one week to another, and from one year to another.

The results of successive visits to a workplace may be plotted on a control chart for prediction purposes. This is a useful means for predicting ahead when an environment is getting out of control, as might happen, for example, with an increase in production or with seasonal fluctuations.

The successive averages are plotted by date. The chart is set up by first considering a sample of, say, 20 visits. A warning line is drawn 2 standard deviations above the grand average, and an action line 3 standard deviations above this average. The standard deviation here is that between the average concentrations from the 20 visits. The warning line should, of course, be at or below the TLV at the outset. Subsequent results should all fall below the warning line. A point falling above this line should be followed by a repeat visit. A repeated point falling above this warning line or a single point falling above the action line indicates that there is good cause for immediate action to be taken to reduce the dust concentration.

A supplementary chart may be drawn up for the range. This, in combination with the control chart for averages, will show whether loss of control is due to an increase in average dust concentration or to dust "floods" occurring within each shift. The latter condition will show up as points above the action line on both charts.

Sampling by the Week

Some particulate sampling methods necessitate a minimum sampling duration of 8 hours in order that the sample can be determined with sufficient sensitivity. In order to collect enough samples in a workshop to be representative of average conditions, it is necessary to have several instruments

being used at the same time and/or to extend each survey over several days.

In such situations a workplace may be defined in terms of the area in which people work on one or a group of identical or similar machines. A workplace can then be assigned its dust category, above or below the hygiene standard, according to the time-weighted average concentration of people working there. This could be determined by sampling continuously or at representative intervals during working hours over one week. The sampling should have been carried out at a minimum of 5 locations, or at a minimum of 5 locations on successive shifts in the area, each location being selected to provide a representative sample of air to which one fifth of the employees are exposed or exposed for a fifth of their time.

In a workplace where the weekly average exposure lies below the TLV, an occasional shift average may exceed the hygiene standard. Accordingly, provided no more than one shift exposure exceeds the hygiene standard and the time-weighted average concentration for the workplace does not exceed the hygiene standard, it may be classified favorably. The k — values given in Table 13-1 may be used for deciding whether the grand average allows a favorable report.

Sampling by the Quarter

Continuous monitoring permits the environment to be assessed at quarterly intervals. Since mineral dust pneumoconiosis are the result of at least some years of exposure, health may be protected provided the quarterly or 6-monthly average mineral dust concentration is below the corresponding TLV. Shorter period surveys or sample durations are really only necessary in these circumstances through the practical inconvenience of the longer period.

A workplace may thus be assigned its category according to the time-weighted average concentration determined by sampling continuously or at representative intervals during the previous quarter.

Time weighted average concentration =

$$\frac{\text{Average concentration during working hours} \times \text{No. of hours worked per quarter}}{520}$$

520

Three months is sometimes an inconveniently long time to wait in uncertainty, such as in a new environment, or in a workplace where use of the mineral has just begun, or airborne dust measurements have not previously been made.

The common situation exists where the mineral is used regularly and is likely to continue in use for some time. In such a situation a procedure is needed which develops into a regular 3-monthly schedule of sampling. However, there are other situations in which the mineral may be used rarely or sporadically or for only a short period, possibly for a few days, with no expectation of repeated use. In these cases, there is a need for rules on the acceptable maximum concentration for short periods.

At a new workplace, in order to give early warning should the time-weighted concentration be especially high, it should first be assigned a

category according to the level of the time-weighted average concentration over a full shift. After one week of sampling it should be reclassified according to the level of the time-weighted average concentration adjusted to 40 hours.

Subsequent reclassification might then be made quarterly, based upon results from samples taken during the previous quarter. Provided no more than one week exposure exceeds the hygiene standard and the average for the workplace does not exceed the hygiene standard, it is classified in the favorable category.

The spacing of the samples over a 13-week sampling period should be planned in advance. The samples should be taken at regular intervals or at times chosen beforehand, whether the duration of each sample is a few minutes, a shift, a week or even 13 weeks. The longer the duration of each sample and the more samples that are taken, the more accurately will the average concentration be estimated. Sufficient assurance that the average concentration lies below a given level would be gained by showing that the upper 90% confidence limit of the average lies below that level. In a workplace where the long-term average concentration lies below the threshold limit value, an occasional quarterly average may exceed the threshold limit value. Accordingly, even though the most recent quarterly average exposure exceeds the threshold limit value, an environment could be classified favorably if the time-weighted average concentration during the last four successive quarters lies below the threshold limit value.

There are workplaces where the conditions change through applying new methods of work, through replacing machines or through changes in the ventilation systems. A workplace that has undergone such changes which may affect its classification should be regarded as a new one. Further, a workplace where the material is used irregularly, or for a few days at a time, or where its regular use cannot be foreseen, should be assigned a category according to the time-weighted average concentration over a single workday.

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