

SIZING METHODOLOGY

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CHARACTERISTICS OF AIRBORNE PARTICLES

The most important single parameter useful in predicting or explaining the behavior of airborne particles is a description of their size. This fact can be appreciated more clearly when the wide range of sizes likely to be present is considered. Particle sizes may range from 10^{-7} cm. in diameter for condensation nuclei to 10^{-3} cm., the upper limit for respirable particles, thus covering four orders of magnitude. If the smallest size is visualized as a steel ball 1 mm. in diameter, then at the same scale, the largest size would be 10 meters in diameter. It would be surprising if these particles obeyed the same laws or indeed if they could be measured using the same instrument. If the relative masses of these two particles is considered, the comparison becomes truly astounding (10^{12}). With the same scale a molecule of air would be less than half a millimeter in diameter and the average distance between molecules of air would be approximately 10 cm. Thus, one could visualize particles smaller than 10 cm. on our scale, for example of the order of 0.1 micrometer (0.1 μ m), floating about with only occasional contact with molecules of air. When contact did occur, however, the exchange of energy in the collision would be sufficient to alter the course of the particle. On the other hand, a large particle on this scale of perhaps a meter in diameter would be bombarded constantly by air molecules and its motion hindered considerably. In this case however, a collision with a single air molecule would probably go unnoticed. Thus, in attempting to describe the behavior of an airborne particle the most important description has to be its size; many characteristics of dust clouds such as rate of settling, agglomeration, Brownian motion, and diffusion must be primarily size-dependent.

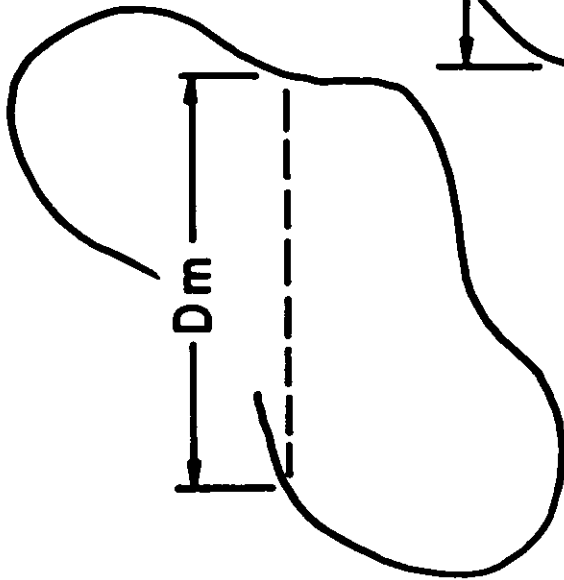
On the other hand, if one wished to compare the behavior of two dust clouds having approximately the same size of particles, other factors could become important. The density of the particles might differ by a factor as high as two or three, and the shape could range from spherical for liquid droplets to needles for fibers or flat platelets in the case of mica or graphite. Certainly these differences would also alter the predicted behavior of the particles.

The hazard of airborne particles results from interaction with the tissue of the lung. In order to reach the deep lung, the particles must pass through the nasopharyngeal region, the trachea, and the bronchi. In each of these regions the air-flow is quite turbulent and larger particles tend

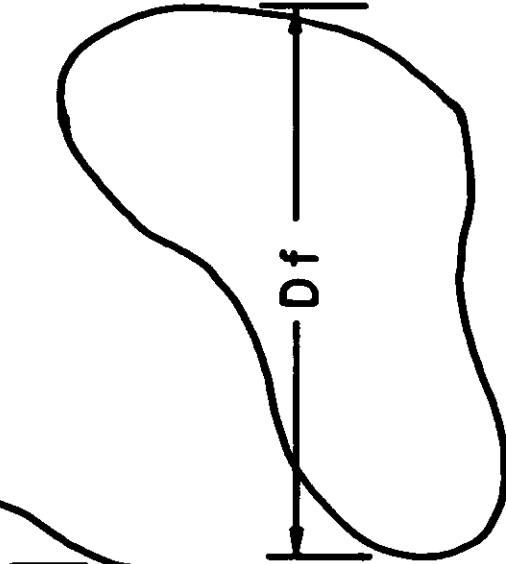
to be removed by impaction. These particles are transported to the mouth by the mucociliary flow, and therefore enter the gastrointestinal tract. Particles smaller than approximately ten micrometers in diameter, however, can penetrate into the deeper regions of the lung and be deposited where the mechanism for removal involves phagocytosis, a much slower process. Thus the size of particles of concern as a health hazard is generally considered to be below 10 micrometers in diameter. The lower size of the respirable range is less well defined. Particles smaller than a few tenths of a micrometer in diameter are subject to Brownian motion and are deposited in the lung by diffusion with reasonable efficiency. Since it would require millions of these small particles to equal the mass of one 10-micrometer particle the actual dose to the lung may be quite small. There are, of course, certain specific cases as radioactive materials where particles smaller than 0.1 μ m in diameter are most important.

Quite apart from physiological considerations there are physical factors which affect the numbers and sizes of particles found in the air. These particles comprise a dynamic system which is constantly changing. Large particles tend to be removed rapidly by sedimentation while smaller ones are likely to agglomerate. In the production of small particles from a bulk material the amount of energy required to reduce relatively coarse material to extremely fine particles may be phenomenal and therefore many industrial processes such as grinding or crushing may be incapable of producing particles smaller than 0.1 micrometers in diameter. Welding operations, on the other hand, produce copious quantities of 0.01 micrometer fumes. Any given sample of airborne dust may therefore contain a wide variety of shapes as well as sizes of particulate matter.

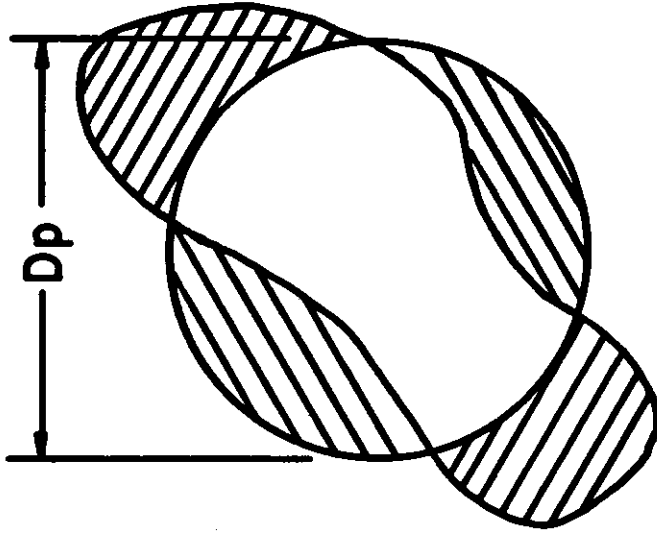
This, of course, makes a description of particle distribution somewhat difficult. If all the particles were of one size, one would merely have to measure that size to define the distribution. If they were all spherical one could measure a sample of the particles and perhaps report an average size. If the shapes are irregular, however, one must first decide what dimension is to be considered as the particle diameter. Three possibilities are shown in Figure 14-1. Martin's diameter is the length of a line which divides the particle into two equal areas. This line could be drawn in any direction for the first particle to be measured, but all other particles should be measured in a direction parallel to the first. If the particles are randomly oriented and a large number



MARTIN'S DIAMETER



FERET'S DIAMETER



PROJECTED AREA DIAMETER

Figure 14-1. Geometric Diameters for Irregularly Shaped Particles

are measured, the direction of measurement is not important. Feret's diameter is the distance between the extreme boundaries of the particle. Again all measurements should be made in the same direction. The projected area diameter is the diameter of a circle having the same cross-sectional area as the particle. Other possibilities would be to measure the longest or shortest dimension of the particle. Estimates of the average size obtained by measuring the shortest diameter would yield the smallest value. Martin's diameter would be followed next by the projected area diameter and Feret's diameter. Measuring the longest dimensions would yield the greatest average diameter. Which then would be nearest to the correct or most useful estimate? Obviously neither the shortest nor the longest dimensions accurately describe the mass of the particles measured although recent work has indicated the smallest dimension may most nearly predict the aerodynamic behavior of fibrous particles. Martin's diameter would seem to underestimate the true size and Feret's diameter would appear to be an over-estimate. The projected area diameter therefore would seem to offer the best estimate of the true size. It is worth noting that for spherical particles all of these estimates would be the same. This statement may take on more significance when one realizes that as particle-size decreases all particles tend to approach the spherical or at least an isometric shape.

STATISTICAL CONSIDERATIONS

A sample of airborne dust will always yield particles of many different sizes and therefore can be called polydisperse. When we consider the behavior of airborne particles, the degree of this polydispersity is usually far more important than factors of shape and perhaps even density. Therefore a simple statement of the average diameter is not very useful in describing these particles. It would indeed be desirable to also be able to describe the degree of polydispersity. If we would assume that the sizes of the particles followed the normal or Gaussian distribution (bell shaped) we could use the powerful techniques of statistics to describe and analyze the distribution¹. Thus we could say that 67% of all the particles had sizes falling between the limits of plus or minus 1 standard deviation from the mean, 95% between plus or minus 2 standard deviations and 99.7% between plus or minus 3 standard deviations. The average size of the distribution would be given simply by:

$$\bar{d} = \frac{\sum_{i=1}^n i N_i d_i}{\sum_{i=1}^n N_i}$$

where \bar{d} is the average size of the distribution, and N_i is the number of particles of size d_i ; the stan-

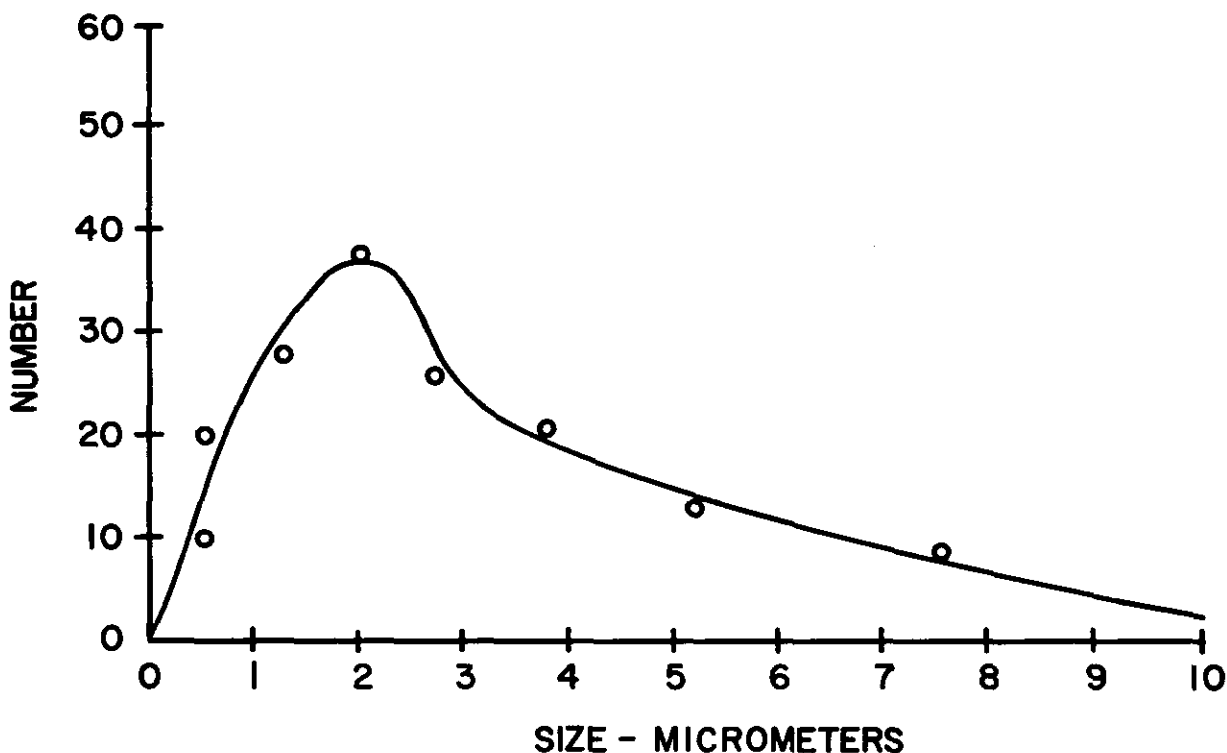


Figure 14-2. Log — Normal Size Distribution

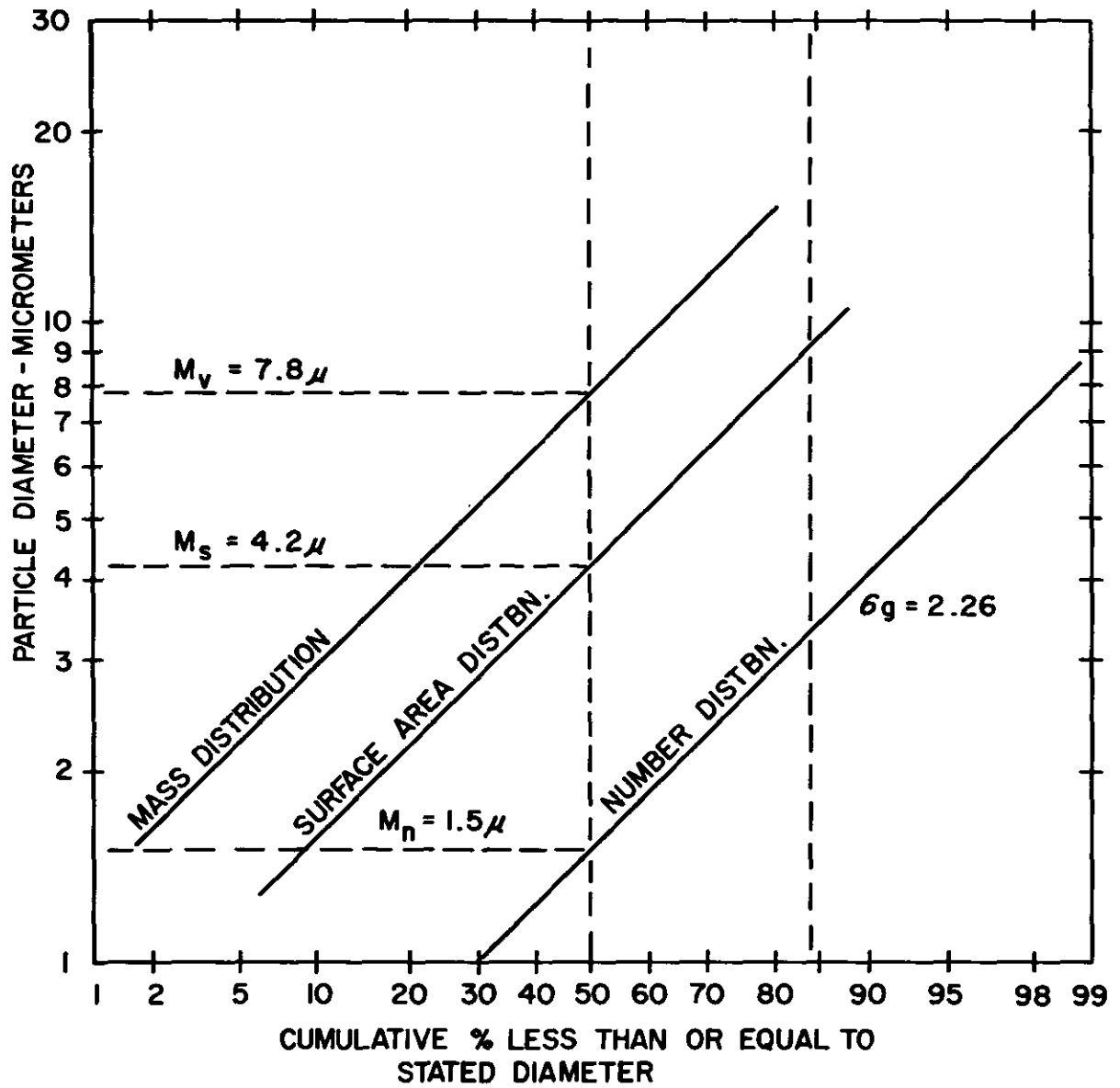


Figure 14-3. Summated Size-Number, Size-Surface and Size-Mass Distributions Plotted on Log-Probability Paper

standard deviation would be a measure of polydispersity:

$$\sigma = \left(\frac{\sum (d_i - \bar{d})^2 N_i}{\sum N_i - 1} \right)^{1/2}$$

Unfortunately, the particle sizes of most aerosols are not normally distributed due to the loss of larger particles by sedimentation and other factors mentioned above. Instead the curve is usually skewed toward the smaller sizes. A typical skewed distribution is shown in Figure 14-2; the data is given in Table 14-1. Hatch² showed, how-

TABLE 14-1: Particle-Size Distribution

size- μm	number	$\sum n$	$\sum \%$
0.5	10	10	5
0.7	22	32	16
1.0	26	58	29
1.4	29	87	43
2.0	37	124	62
2.7	28	152	76
3.8	22	174	87
5.4	14	188	94
7.7	8	196	98
10.9	4	200	100

ever, that if one plotted the logarithm of the particle size instead of the actual size the result closely approximated a normal distribution. Thus, we can say that:

$$\bar{d} = \log^{-1} \left(\frac{\sum N_i \log d_i}{\sum N_i} \right)$$

and

$$\sigma = \log^{-1} \left(\frac{\sum (\log d_i - \log \bar{d})^2 N_i}{\sum N_i - 1} \right)^{1/2}$$

We are saying that the log-normal distribution provides a reasonably good approximation of the particle-size distribution usually found in airborne dusts. It should be noted, however, that other possibilities do exist and such occurrences as bimodal distribution or the mixing of dusts from two entirely different sources (smoke and dust for instance) happen frequently.

If we accept the log-normal distribution as representing the actual size-distribution of airborne particles, we can simplify our calculations by resorting to a graphical solution. If we plot the summated size-distribution on logarithmic-probability paper, the result should be a straight line if the assumption of a log-normal distribution is correct. The lower line of Figure 14-3 is such a plot of the data from Figure 14-2. From this graph we can read directly the median or 50% size. In the illustration 50% of the particles are larger than 1.5 micrometers and 50% are smaller. We can also read any other points on the curve. 80% of the particles measured were smaller than 3.0 micrometers in diameter and 95% were smaller

than 5.0 micrometers. As a measure of the polydispersity we can also find the standard deviation by dividing the 84.13% size by the 50% size, in this case 3.4 micrometers, divided by 1.5 micrometers gives a standard geometric deviation, σ_g , of 2.26, a dimensionless number. The same value for σ_g could, of course, be obtained from the other end of the curve by dividing the 50% size by the 15.87% size. The standard geometric deviation therefore represents the slope of the line and along with the median size is sufficient to describe the distribution.

The log-probability distribution described above is expressed mathematically as follows:

$$F(d) = \frac{\sum N}{\log \sigma_g \sqrt{2\pi}} \exp. \left[- \frac{(\log d - \log \bar{d}_g)^2}{2 \log^2 \pi_g} \right]$$

where $F(d)$ is the frequency of occurrence of the diameter d , $\sum N$ is the total number of particles, σ_g is the standard geometric deviation and \bar{d}_g is the geometric mean diameter. This function predicts the existence of all sizes of particles from zero to infinity. Since the number of particles contributing to the extremes of the distribution is small, the confidence bands around the two ends of the line are wide and become narrowest at the 50% size. It can be shown that in order to estimate the median size within 10% of the true mean with 95% confidence, a minimum of 200 particles must be measured. If, on the other hand, we wished our estimate of the median size to be within 5% of the true mean with the same degree of confidence, we would have to measure at least 1000 particles. In the example given above we estimate the median size to be ± 0.15 micrometers. For most purposes this is an adequate estimate and therefore the measurement of 200 particles is sufficient.

The number-size distribution of the particles having been established, other parameters of interest can also be determined. If we wished to examine the distribution of mass among these particles, assuming a constant density, we could multiply the frequency of occurrence of particles in each of our size ranges by the cube of the average diameter for that range and summate these weighted frequencies. This is shown in Table 14-2.

TABLE 14-2: Size-Mass Distribution Data

size	n	d	d ³	d ³ n	$\sum d^3 n$	$\sum \% d^3 n$
0.5	10	0.25	0.02	0.2	0.2	0.0
0.7	22	0.6	0.22	4.9	5.1	0.0
1.0	26	0.85	0.61	16.	21.1	0.3
1.4	29	1.2	1.7	46.	67.1	0.8
2.0	37	1.7	6.1	230.	297.1	3.0
2.7	28	2.3	10.2	290.	587.1	7.0
3.8	22	3.2	32.0	700.	1287.1	16.0
5.4	14	4.6	93.0	1300.	2587.1	33.0
7.7	8	6.5	260.	2100.	4687.1	59.0
10.9	4	9.3	790.	3200.	7887.1	100.0

Plotting these data as summated percentages on log-probability paper produces a curve which represents the mass distribution of the aerosol. This is plotted as the upper curve of Figure 14-3. From this curve we can obtain the mass-median diameter or the size below or above which half of the mass of the particles would occur. It should be noted that had the density of the particles been included in weighting each frequency range in the above calculation, the density factor would have cancelled when dividing through by the grand summation to reduce the data to percentages. It is also apparent that the standard geometric deviation of the size-mass distribution (the slope of the line) is identical to that of the number distribution. The size-mass distribution is often useful in predicting the actual dose to the lung resulting from the inhalation of a given amount of dust or the weight of material collected by a filter or other collection device which is efficient only for particles larger than a given size.

A similar technique can be used to describe the distribution of surface-area for the particles in question, assuming spherical symmetry of the particles. In this case the number-frequency of particles in each range is weighted by multiplying by the square of the average diameter of the range. This has been done in Table 14-3 and plotted as

TABLE 14-3: Size-Surface Distribution

size	n	d	d ²	d ² n	Σd ² n	Σ% d ² n
0.5	10	0.25	0.06	0.6	0.6	0.04
0.7	22	0.6	0.36	7.9	8.5	0.6
1.0	26	0.85	0.72	19.	27.5	2.0
1.4	29	1.2	1.4	41.	68.5	6.8
2.0	37	1.7	3.6	140.	208.5	14.8
2.7	28	2.3	5.3	149.	357.5	25.3
3.8	22	3.2	10.0	220.	577.5	40.8
5.4	14	4.6	20.1	180.	757.5	53.5
7.7	8	6.5	40.2	320.	1077.5	76.0
10.9	4	9.3	83.0	332.	1409.5	100.0

the middle line of Figure 14-3. The surface-area distribution is sometimes useful in comparing or predicting surface related phenomena such as the scattering of light, adsorption of vapors or the reaction of insoluble particles with biological tissues. Hatch² has proposed equations which permit the direct calculation of the mass-median (M_g) and surface-median (S_g) diameters from the size-median diameter without the weighting procedures described above. The most important of these is given below:

$$\log M_g = \log d_g + 6.9078 \log^2 \sigma_g$$

Since σ_g is the same for the mass and number distributions, calculation of M_g permits the curve describing the entire mass distribution to be drawn immediately.

MEASUREMENT TECHNIQUES

The technique of measuring the size of airborne particles has to begin with the selection of

the sampling instrument. The factors which must be considered to prevent bias of the sample in favor of either larger or smaller particles have been described in Chapter 13. Once a representative sample has been obtained a specimen of this must be prepared for observation and measurement using a standardized technique. Care must be taken that the preparation of this specimen and the measurement technique itself does not introduce bias and destroy the representative nature of the specimen.

Optical Microscopy

In order to serve as a standard method in the field of Industrial Hygiene, a technique should be suitable for use generally in laboratories across the nation. This may preclude the use of certain exotic instruments that are so expensive or complicated that they are found only in a few highly specialized laboratories. For the counting and sizing of airborne dust particles, the optical microscope is usually available and can be operated by a trained technician. For particle-size analysis any good quality clinical microscope is adequate. Because the size of the smallest particles to be measured will approach the theoretical limit of resolution of the optical system, the illumination either built into the microscope or provided by the operator should meet the requirements of either Kohler or critical illumination. Thus the operator must have some knowledge of the optical system that he will use.

The optical microscope³ is comprised of five basic components: (1) the light source, (2) the condenser lens which focuses the light on the specimen, (3) the specimen stage which holds and makes possible movement of the specimen, (4) the objective lens which produces an intermediate and magnified image of the object and (5) the ocular which further magnifies the intermediate image and presents it as a virtual image to the eye. The heart of the instrument is the objective lens, for the quality of the final image can be no better than that of the intermediate image produced by this lens. The quality of the image is better described as the resolution or fineness of detail that is preserved by this lens. The limit of resolution is given by the Abbé equation:

$$d = \frac{0.61\lambda}{\eta \sin \alpha}$$

where d is the shortest distance separating two fine lines at which the two lines can still be distinguished; λ is the wave-length of the light used; η is the index of refraction of the medium between the specimen and the lens; and α is the half angle subtended between the axis of the optical system, the periphery of the lens and the specimen. It is, therefore, the maximum angle through which the lens can receive light from the specimen. This angle, of course, can not exceed 90° or the specimen would have to be inside of the lens. The sine of α can approach 1.0 as a limit and is usually 0.94 for a high magnification lens. The index of refraction of the medium is also limited, being 1.0 for air, 1.33 for water and 1.515 for the usual immersion oils. The product of the index of refraction and the sine of α is called the numerical

aperture (N.A.) of the lens. This will range from 1.25 for a high magnification (97x) oil immersion lens to less than 1.00 for a low power lens. The wavelength of the light used is limited to the visible spectrum. Thus the shortest visible wavelength will be at the violet end of the spectrum and of the order of 400 millimicrons. Substituting these values in the Abbé equation shows that the theoretical limit of resolution for any optical lens must be approximately $200m\mu$ ($0.2 \mu m$). In order to attain this, however, the full numerical aperture of the lens must be utilized, and this is possible only with a condenser lens having a high numerical aperture and either Kohler or critical illumination. In addition to this the objective lens must be of high quality and corrected for chromatic aberrations for three colors. Such a lens is called an apochromatic objective.

The quality of the ocular is somewhat less important. The limit of resolution of the eye is usually taken to be approximately 0.1 mm. If the finest detail in the specimen is magnified to 0.1 mm, it will be discernible to the eye. Therefore, the finest detail resolvable by the objective lens ($0.2 \mu m$) has to be magnified only 500 times in order to be visible. If the high-dry objective (usually 46x) were used, a 10x ocular would accomplish this since the overall magnification would be 46×10 or 460. Certain refinements which are available in oculars such as wide field, flat field (for photographic purposes), high eyepoint (for people who wear glasses) and higher magnifications (15-20x) may be desirable and convenient even though they may contribute little to actual improvement of the image.

Preparation of Specimens

Given a satisfactory optical system, the specimen must be suitably prepared for observation and measurement. The sample may have been obtained in the same manner as described in Chapter 13 for dust counting, with either the midjet impinger or a membrane-filter. In either case the sample would be prepared in the same manner in the Dunn cell or the haemocytometer or by using the proper immersion fluid to render the membrane-filter transparent. There is no need to relate the sample used for size analysis to any particular volume of air, and it is often convenient, therefore, to collect separate samples for size analysis in order to obtain a greater number of particles. Occasionally, one may be working with a bulk sample of material, and in this case great care must be taken to spread a representative sample uniformly on a microscope slide in such a manner that bias is not introduced by selectively retaining the small particles on the glass surface. It must be remembered that the collection of the sample resulted in the concentration of the particles either on a surface or in a liquid and thus may have resulted in agglomeration or other change from the airborne state. It may, therefore, be necessary to subject the particles to a deagglomeration procedure such as insonation in an ultrasonic generator prior to the preparation of the final specimen. In general it is felt that collection

on the membrane filter causes less change from the airborne state than other methods.

Reticles and Calibration

When the specimen has been properly prepared on the microscope slide it must be focused in the field of the microscope. Actual measurement then consists of superimposing on the field a suitable scale, reticle or measuring device. The first device that was used intensively for this purpose was the Filar micrometer. It is, in fact, a substitute eye piece which superimposes on the field a scale comprised of 100 units. Part of this scale is a movable verticle cross-hair which is controlled by a micrometer screw thread connected to a drum dial. The circumference of the drum dial is divided into 100 units and can be read to 0.1 unit by means of a vernier. One complete rotation of the drum dial (100 units) moves the cross-hair one division of the field scale. In practice the cross-hair must be moved in one direction until it just touches one boundary of the particle to be measured. A reading of the drum dial is taken and the traverse continued until the other side of the particle is reached. The difference between the two drum dial readings gives the Feret's diameter of the particle in units. A minimum of 200 particles are measured in this manner.

The Filar micrometer, however, is a tedious instrument to use. The measurement of Feret's diameter obtained with this instrument is less representative as the particles depart from isometric. For these reasons reticles which are more easily used have come into favor.

The most common of these is the Porton reticle which is named after the research group in England that was responsible for its design. It consists of a photographically reduced and reproduced transparent grid which is mounted exactly in the focal plane of either the Hygens or the Ramsden ocular. The grid is thus superimposed on the field of the microscope. A picture of this grid superimposed on a dust specimen is shown in Figure 14-4. It consists of a large rectangle one half of which is divided into six smaller rectangles. Along the top and bottom of the rectangle are a series of circles or dots of increasing size. The diameter of each dot is larger than the previous one by the square-root of two. Thus the diameter of any circle in Porton-units is given by:

$$d = \sqrt{2^n}$$

where n is the number of the circle. The height of the large rectangle is 100 units and its length is 200 units. Either the length or height can be calibrated against a stage micrometer to determine the value of one Porton unit in micrometers. Measurements are made by comparing the size of the particles with the circles to find the circle that would completely enclose the particle. This can be done visually and without superimposing the circle on the particle by moving the stage of the microscope. Therefore, all particles contained in the area defined by the six smaller rectangles can be sized before moving on to a new field. This tends to minimize the possible bias of sizing only the larger particles. There is, of course, a natural tendency to equate projected areas of the particles

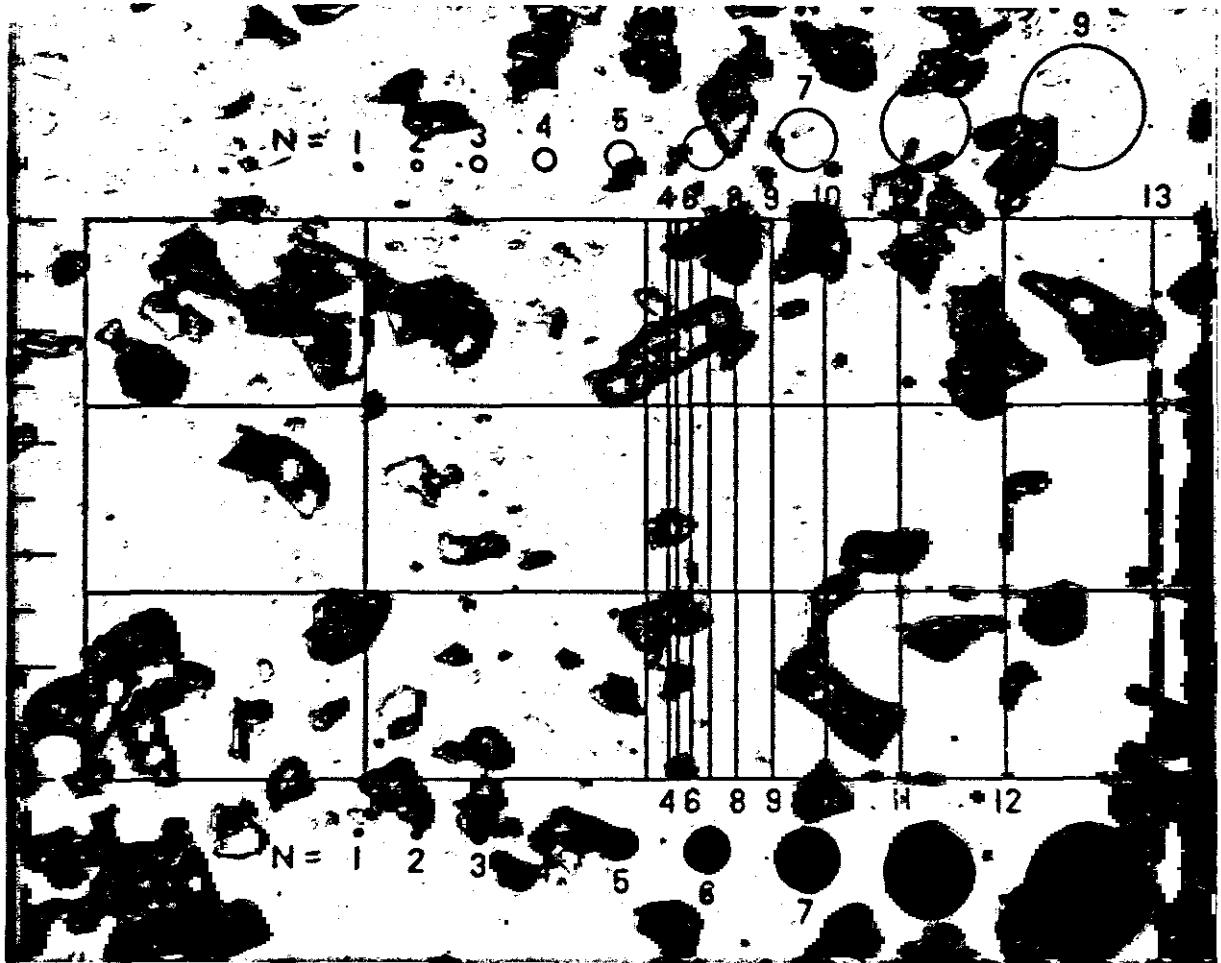


Figure 14-4. The Porton Reticle Superimposed on a Dust Field

and circles. In many cases this projected area diameter is more desirable than Feret's diameter. The entire analysis can be done by one operator and only one reading is required for each measurement.

The calibration of any reticle placed in the optical system consists of comparing that reticle to a stage micrometer substituted for the actual specimen and using exactly the same optics that are used for measurement. Thus one cannot calibrate the optical system using the 10x objective and then switch to the 46x or oil immersion objective to size the particles. Nor can a calibration be transferred from one microscope to another even if similar lenses are used. The tube length of the microscope on older models can sometimes be adjusted to make the calibration result in even numbers. It is good practice, therefore, to include the calibration data with each size analysis and also, if possible, a photo-micrograph superimposing the reticle directly on the image of the stage micrometer so that the reader can see for himself that the calibration is at least approximately correct.

RELATED TECHNIQUES

Although the standard method for particle-size analysis with the optical microscope is usually adequate to describe the implication to health of airborne particles, there may be special situations which require the application of more sophisticated techniques. Smoke and fume particles may well lie below the limit of resolution of the optical system. Continuous monitoring using automated instrumentation and an immediate readout may be desired. It is appropriate therefore to describe a few of the techniques which may be useful in research or specialized field application.

The Electron Microscope⁴

Because of the short wavelength associated with a beam of electrons, the theoretical limit of resolution of the electron microscope is extremely small. In practice resolution between 10 and 20 angstrom units is readily attainable. Physically the electron microscope is quite analogous to the optical microscope. It consists of a heated filament which is the source of electrons, a condenser lens, a mechanical stage, an objective lens, a projector lens and a fluorescent screen which converts the

electron image into visible light. Electrons, having both mass and charge, have a short path length or penetrating power through any medium, and a high vacuum is necessary if they are to travel the length of the microscope column. Since the specimen must be placed in the vacuum, only dry non-volatile materials can be examined. These must be extremely thin (0.1μ or less) and be supported on a thin film of low density material. Classically, films of collodion or Formvar (R) approximately 100 \AA thick are used to support the specimen. These films in turn are supported on 200 mesh grids of copper or stainless steel $\frac{1}{8}$ in. in diameter.

Preparation of the specimen consists of transferring the airborne particles which may have been collected by a technique described in Chapter 13 to a previously prepared film and grid. Because of the high magnification of the electron microscope and consequently the small field to be observed, the preparation of the specimen without introducing bias is more critical than in the case of optical microscopy. The particular technique will depend on the method that was used to collect the sample. If the dust sample was collected in water by impingement, a drop of the particulate suspension may be placed on the grid and allowed to evaporate to dryness. If a bulk sample of insoluble dust is to be examined, a dilute suspension of the particles in distilled water may be prepared. Insonation by ultrasonic energy is often useful to deagglomerate the particles. If the sample has been collected on the membrane filter, it may be transferred to a grid by placing a small piece of the filter face down on a Formvar (R) grid and removing the filter media by solution in ethyl acetate as described by Fraser.⁵ Airborne dusts or fumes may be deposited directly on the filmed grids by electrostatic or thermal precipitation. In each case, however, the size distribution may be altered.⁶ Shadow-casting, the technique of evaporating a thin film of metal on the specimen from a low angle, can be used effectively to enhance the detail and increase the contrast of any of the above preparations.

Impaction Devices

Impingement implies the collection of particles in a liquid medium. Impaction, on the other hand, describes the deposition of particles on a dry (or adhesive coated) surface. If air moving at high velocity is forced to change direction abruptly by an obstacle, particles entrained in the air may be unable to follow the air stream and, due to their momentum, may collide with the barrier. If in a single instrument air is drawn through a series of orifices of decreasing size, the velocities attained will increase as the cross-sectional area of the orifice decreases. With increasing velocity, smaller particles will be forced to collide with an obstacle such as a microscope slide placed in the path of the jet. Only large particles will be deposited on the first stage of this device while smaller particles will deposit on subsequent stages. Such a device is called a "cascade impactor" and is used to collect particles in various size fractions. It should be noted that the range of sizes collected on each stage depends on the density and shape of the particles as well as the diameter and therefore

represents the aerodynamic behavior of the particles. The number or weight of particles collected on each stage can be determined by counting, using an optical microscope, by weighing or by chemical analysis. If the density of the dust is known and a size-distribution is obtained for each stage, a relationship can be calculated which will permit one to predict what size of particles will be deposited on each stage for dusts of different densities. For subsequent analyses it is only necessary to determine the mass of material collected on each stage in order to describe the particle-size distribution. The volume flow of air through the device must of course, be kept constant. Because of the varieties of sizes, shapes and densities of airborne particulates inertial impactors are usually calibrated with reference to a standard material. If this standard consists of spherical particles having a density of 1 gm/cc (polystyrene latex balls), then in subsequent analyses particles of irregular shapes and varying densities will be classified according to their aerodynamic equivalence to these unit density spherical particles.

A recent innovation has been the Anderson sampler which is a multi-orifice cascade impactor. A number of orifices of the same size are arranged in concentric circles on each stage. Orifice diameters decrease for each succeeding stage and the diameters of the circles in which they are arranged are staggered on alternating plates; thus the orifice plate serves as the collecting plate for the preceding stage. This design has a number of advantages over single jet impactors. The multiple jets permit large air flows and the collection of larger samples. The plate construction can be quite thin and light-weight permitting more sensitive weighing. The instrument has fewer parts and each time the plates are cleaned the jets are also cleaned. The orifices are circular and therefore the machining can be more precise and the calculations simpler. There is a minimum size of particle which can be collected by inertial impaction. This is the smallest particle that can be collected when the air passing through the jet reaches sonic velocity. This maximum velocity limits the collection of particles by this technique to those larger than a few tenths of a micrometer in diameter. It may be desirable to follow the cascade impactor with a membrane filter or an electrostatic precipitator to collect smaller particles.

Centrifugal Collectors

Centrifugal classifiers or cyclone separators have been used commercially for many years to provide aerodynamically sized fractions of bulk materials. In sampling technology they are generally used as pre-filters to eliminate particles larger than the respirable size. In a few instances the technique has been used to provide information concerning the size of airborne particles.

When an air stream containing dust is forced to follow a circular path, the particles experience a centrifugal force which tends to move them across the stream lines toward the outer wall of the vessel or duct. The centrifugal force increases as the radius of curvature decreases. In the cyclone collector the air stream is introduced tan-

gentially into the widest section of a cone and forced to follow a spiral path of decreasing radius of curvature to the apex of the cone. Thus the centrifugal force increases to a maximum at which point all particles larger than a minimum size will intersect the wall of the cone and be collected. The minimum size that will be collected depends on the dimensions of the cone, the inlet velocity of the air and the distance that the particle must travel perpendicular to the direction of the air flow in order to reach the side. The greatest efficiency will be provided by a long narrow cone operating at high air velocity.⁷ For any given cyclone the minimum size can be increased or decreased by varying the air velocity. Goetz designed an aerosol spectrometer which passed the air in a narrow channel between two concentric rotating cones so that the larger particles were eliminated at the larger end and smaller ones were deposited near the apex. By examining the surface of the outer cone and measuring the distance between the point of inlet and point of deposition, and knowing the speed of rotation and therefore the centrifugal force, he was able to calculate the aerodynamic size of the particle. This instrument was particularly useful in investigating the effect of air, temperature and humidity on the size of particles.

Light Scattering

In the search for automated techniques, instruments which can detect light reflected or scattered from the surface of airborne particles have been developed. A major advantage of such a technique is that the particles need not be collected but are examined in their airborne state. These instruments may respond to light scattered by all particles contained in a fixed volume or the light from individual particles. While the former are sensitive to changes in the number of particles, they are of little use in determining the size of the particles since many small particles may scatter the same amount of light as a few larger ones. Since the light from a discrete particle is reflected from its surface, it can be related to its size. This, however, is not a simple relationship since light may also be diffracted by the edge of the particle or adsorbed a specific wavelength by colored particles. This is further complicated when the particle-size approaches the wavelength of the light. Thus the intensity of light scattered depends on the angle of observation relative to the direction of the incident beam, the greatest intensity usually being observed in the forward direction or looking back toward the light source. The original theory of light scattering was described by Rayleigh for large particles and by Mie for small particles approaching the wavelength of light.⁸ Mathematical functions and tables have been constructed to describe the light scattered at various angles by transparent isotropic spheres. This is, of course, most useful, but one has only to consider the effect of particle shape ranging from flat platelets to long fibers to imagine the complexity of the practical situation. In spite of this, light-scattering devices can be calibrated empirically for a particular dust with a standard chemical or optical method and can be extremely useful for

routine monitoring of clean rooms, animal inhalation chambers, certain industrial processes and testing of filter penetration.

Measurement of Electrical Charge

Airborne particles undergo a continuous bombardment of approximately 10^9 collisions per second by the molecules which comprise the air. If a portion of these molecules are electrically charged ions, this charge will be transferred to the particles and if the ions are unipolar the particles assume this polarity. Due to the coulombic force of repulsion between like charges this charge will be distributed on the surface of the particles. The first ions which approach the neutral surface experience no repulsive force but as the total charge on the particle increases additional ions approaching the surface must overcome a force of repulsion if contact is to be made with the surface. It is apparent that there will be a maximum number of charges that a particle can accept for a given concentration and energy of the ions in its environment. This maximum will be a function of the surface area of the particle.

A charged particle which finds itself in an electrostatic field between two plates will migrate toward the plate of opposite polarity. The velocity that it attains will depend on the field strength as well as the charge to mass ratio of the particle. Since the ratio of the surface to the mass is greatest for small particles, this will also be true for the charge to mass ratio. Small particles will therefore have a greater mobility in the electrical field than larger ones.

In recent years instruments have been developed to take advantage of the phenomena to classify particles according to their size.⁹ The airborne particles are first subjected to a dense concentration of unipolar ions. Maximum charging of the particles can usually be attained in a few milliseconds. They are then passed between a series of plates each of which subjects the particles to an electrostatic field of increasing strength. Thus the free ions will be eliminated by the first field while small charged particles will be collected by the next, and larger particles by subsequent plates. A sensitive electrometer connected to each of the plates can measure the electrical current collected at each stage. Thus the fraction of the current flowing in each stage becomes a measure of the number of particles of each size that comprise the overall particle-size distribution.

The major advantage of the charge measuring technique is its ability to cope with the total range of particle sizes from air ions to large dust particles and its great sensitivity for the smallest particles. The equipment, however, is extremely complicated and expensive, and it is not now feasible to use it as a field instrument.

SUMMARY

Information concerning the distribution of airborne particles can be obtained by means of a variety of methods and techniques which measure any one of several physical properties of the particles. The interpretation of the results from measuring different physical properties may be quite different and not necessarily comparable.

It is most important, therefore, that the sampling device, the measurement technique, and the parameter measured be chosen with careful consideration of the application to be made of the data. It is often true that as the sophistication of the instrumentation increases, the actual parameters measured become more obscure. The industrial hygienist should be thoroughly familiar with the basic concepts and the relatively simple techniques that can be used for estimating the size of airborne particles, since these provide a basis for standardization of automated equipment and a solution to problems when such equipment is not available.

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Measuring System for the 0.015 to 1 μm Size Range," *Tellus* 18, 573 (1966).

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Periodic Publications

1. Journal of the American Industrial Hygiene Assoc.
2. Journal of the Air Pollution Control Assoc.
3. Staub
4. British J. Applied Physics
5. Environmental Science and Technology
6. Review of Scientific Instruments
7. Health Physics
8. British Journal of Industrial Medicine
9. Annals of Occupational Hygiene
10. Journal of Colloid Science

SAMPLING AND ANALYSIS OF GASES AND VAPORS

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and

Robert G. Keenan

INTRODUCTION

This chapter deals principally with manual methods of sampling and analysis of industrial atmospheres for gaseous and vaporous contaminants (see Chapter 10 for a discussion of the "General Principles in Evaluating the Occupational Environment" and Chapter 16 for the discussion on "Direct Reading Instruments for Determining Concentrations of Aerosols, Gases and Vapors").

For industrial hygiene purposes, a substance is considered to be a gas if this is its normal physical state at room temperature and atmospheric pressure; it is called a vapor if, under the environmental conditions, a conversion of its liquid or solid form to the gaseous state results from its vapor pressure affecting its volatilization or sublimation into the atmosphere of the container, the process equipment, or the workroom. In this chapter the term "gaseous" is used therefore in a general sense in discussing gases or vapors.

Basic Sampling Techniques

There are two basic methods for the collection of gaseous samples. The first involves the use of a gas collecting device, such as an evacuated flask or bottle, to obtain a definite volume of an air-gas mixture at a known temperature and pressure. This type of sample is called a "grab" or "instantaneous" sample as it is collected almost instantaneously, i.e., usually within a few seconds to 1-2 minutes maximum, and is thus representative of the atmospheric conditions at the sampling site at a given point in time. This method is used when the atmospheric analyses are limited to such gross contaminants as mine gases, sewer gases, carbon dioxide and carbon monoxide (above 0.2 percent) and other situations where the concentrations of contaminants are in the percentage range. However, with the increased sensitivity of modern gas chromatographic, infrared and other analytical techniques, instantaneous sampling of ever lower concentrations of atmospheric contaminants is becoming more feasible. The collectors are resealed immediately after sampling to prevent any losses of the sample by diffusion.

The second method for the collection of gaseous samples involves the passage of a known volume of air through an absorbing or adsorbing medium to remove the desired contaminants from the sampled atmosphere. This technique provides a sample of the atmosphere over a recorded time period and is termed "integrated sampling." The contaminant which is removed from the air stream becomes concentrated in/on the collecting me-

dium; the sampling period is chosen to permit the collection of a sufficient quantity of the contaminant for the subsequent analyses.

Sampling Criteria

Whereas airborne particulate substances are readily scrubbed or filtered from sampled air streams due to their larger physical dimensions and to the operation of agglomerative, gravitational or inertial effects, gases and vapors form true solutions in the atmosphere and thus require either sampling of the total atmosphere using a gas collector or the use of a more vigorous scrubbing technique to separate the gas or vapor from the surrounding air molecules. Selected sampling reagents which react chemically with contaminants in the air stream can improve the collection efficiencies of the sampling procedures. In devising an integrated sampling scheme, it is essential to consider the following basic requirements:

1. Provide an acceptable efficiency of collection for the contaminant(s) involved;
2. Maintain this efficiency at a rate of air flow which can provide sufficient sample for the intended analytical procedure(s) in a reasonable and acceptable period of time;
3. Retain the collected gas or vapor in a chemical form which is stable during transport to the laboratory or other analytical site;
4. Provide the sample in a form which is suitable for the analytical procedure(s);
5. Require minimal manipulation in the field;
6. Avoid the use of corrosive or otherwise hazardous sampling media if possible.

Whereas most of these criteria are self-explanatory, some elaboration on the first and second is desirable. It is extremely important that the collection efficiency of a sampling system be known, either from published, well-documented data, as summarized in Table 15-1 for a variety of common contaminants found in industrial atmospheres, or as a result of an independent evaluation as an essential part of planning a future survey. In making such an evaluation, known concentrations of gases and vapors must be prepared (see Chapter 12) and used in a dynamic or static test system to determine the efficiency of the proposed sampling device. The efficiency must be defined in terms of such variables as the type of scrubber, porosity of frits used in the scrubber, size of scrubber, the height, volume, nature, and temperature of the collecting medium, rate of air flow, stability of the sample during collection, losses by adsorption on the walls of the probe, connecting

TABLE 15-1
Collection and Analysis of Gases and Vapors

Gas or Vapor	Sampler	Sorption Medium	Air Flow (L/m)	Minimum Sample (L)	Collection Efficiency	Analysis	Interferences	Ref.
Ammonia	Midget Impinger	25 ml 0.1N Sulfuric Acid	1-3	10	+ 95	Nessler Reagent	—	(13)
	Petri Bubbler	10 ml of above	1-3	10	+ 95	" "	—	
Benzene	Glass Bead Column	5 ml Nitric Acid	0.25	3-5	+ 95	Butanone Method	Other Aromatic Hydrocarbons	(15)
Carbon Dioxide	Fritted Bubbler	10 ml 0.1 N Barium Hydroxide	1	10-15	60-80	Titration with 0.05N Oxalic Acid	Other Acids	(13)
Ethyl Benzene	Fritted Bubbler	15 ml Spectrograde Isooctane	1	20	+ 90	Alcohol Extraction, Ultraviolet Analysis	Other Aromatic Hydrocarbons	(26)
	or Midget Impinger	" "						
Formaldehyde	Fritted Bubbler	1% 10 ml Sodium Bisulfite	1-3	25	+ 95	Liberated Sulfite Titrated, 0.01 N Iodine	Methyl Ketones	(13)
Hydrochloric Acid	Fritted Bubbler	0.005 N Sodium Hydroxide	10	100	+ 95	Titration 0.01 N Silver Nitrate	Other Chlorides	(13)
Hydrogen Sulfide	Midget Impinger	15 ml 5% Cadmium Sulfate	1-2	20	+ 95	Add 0.05 N Iodine, 6N Sulfuric, back titrate 0.01 N Sodium Thiosulfate	Mercaptans, Carbon Disulfide, Organic Sulfur Compounds	(13)
Lead, Tetraethyl, Tetramethyl	Dreschel Type Scrubber	100 ml 0.1M Iodine Monochloride in 0.3N Hydrochloric Acid	1.8-2.9	50-75	100	Dithizone	Bismuth, Thallium, Stannous Tin	(27)
Mercury, Diethyl and Dimethyl	Midget Impinger	15 ml of above	1.9	50-75	91-95	Same as Above	Same as Above	
	Midget Impinger	10 ml 0.1M Iodine Monochloride in 0.3 N Hydrochloric Acid	1-1.5	100	91-100	Dithizone	Copper	(28)
Nickel Carbonyl	Midget Impinger	15 ml 3% Hydrochloric Acid	2.8	50-90	+ 90	Complex with alpha-Furildioxime	—	(29)

TABLE 15-1 (cont'd)
Collection and Analysis of Gases and Vapors

Gas or Vapor	Sampler	Sorption Medium	Air Flow (L/m)	Minimum Sample (L)	Collection Efficiency	Analysis	Interferences	Ref.
Nitrogen Dioxide	Fritted Bubbler (60-70 micron pore size)	20 - 30 ml Saltzman Reagent*	0.4	Sample until color appears Probably 10 ml of Air	94-99	Reacts with Absorbing Solution	Ozone in 5 fold excess Peroxyacyl Nitrate	(30)
Ozone	Midget Impinger	1% Potassium Iodide in IN Potassium Hydroxide	1	25	+95	Measure Color of Iodine Liberated	Other oxidizing agents	(31)
Phosphine	Fritted Bubbler	15 ml 0.5% Silver Diethyl Dithiocarbamate in Pyridine	0.5	5	86	Complexes with Absorbing Solution	Arsine, Stibine, Hydrogen Sulfide	(32)
Styrene	Fritted Midget Impinger	15 ml Spectrograde Isooctane	1	20	+90	Ultraviolet Analysis	Other Aromatic Hydrocarbons	(26)
Sulfur Dioxide	Midget Impinger, Fritted Rubber	10 ml Sodium Tetrachloromercurate	2-3	2	99	Reaction of Dichlorosulfitomercurate and Formaldehyde-para-rosaniline	Nitrogen [#] Dioxide, Hydrogen ^{**} Sulfide	(33)
Toluene Diisocyanate	Midget Impinger	15 ml Marcali Solution	1	25	95	Diazotization and Coupling Reaction	Materials containing Reactive Hydrogen attached to Oxygen (phenol) Certain other Diamines	(12)
Vinyl Acetate	Fritted Midget Impinger and simple Midget Impinger in Series	Toluene	1.5	15	+99 (84 with fritted bubbler only)	Gas Chromatography	Other Substances with same retention time on Column	(34)

* 5 gram sulfanilic
140 ml glacial acetic acid
20 ml of 0.1% aqueous N-(1-naphthyl) ethylene diamine

Add sulfamic acid after sampling.
** Filter or centrifuge any precipitate.

tubing or collecting device which may necessitate a rinsing with a special reagent to remove the adsorbate which must then be added to the collected portion in the sampling device.

The collection of sufficient sample for the intended method of analysis is a matter which must be discussed by the field and laboratory personnel jointly when the survey plans are made. The field men must discuss as fully as possible with the chemists the nature of the processes involved in the survey so they may select the best combination of sampling and analytical methods to meet the sensitivity requirements of the analytical method, minimize the effects of potential interferences and complete each sampling within a time period which is consistent with the cyclic nature of processing operations or with the exposure conditions (see Chapter 10).

INSTANTANEOUS OR GRAB SAMPLING

Numerous types of devices are used in instantaneous or "grab" sampling to obtain a definite volume of air within a gas collector. These include vacuum flasks, vacuum bottles, gas- or liquid-displacement type collectors, metallic collectors, glass bottles, syringes and plastic bags. Air samples must be collected with these devices at a known temperature and pressure to permit the reporting of the analyzed components in terms of standard conditions, normally 25°C and 760 mm of mercury for industrial hygiene purposes.

Grab samples are collected usually where gross components of gases in air such as methane, carbon monoxide, oxygen, and carbon dioxide are to be analyzed. The samplers should not be used for collecting reactive gases such as hydrogen sulfide, oxides of nitrogen and sulfur dioxide since there may be a reaction with dust particles, moisture, wax sealing compound or glass which would alter the composition of the sample. It is preferable when reactive substances are collected in grab samples that the analyses be made directly in the field.

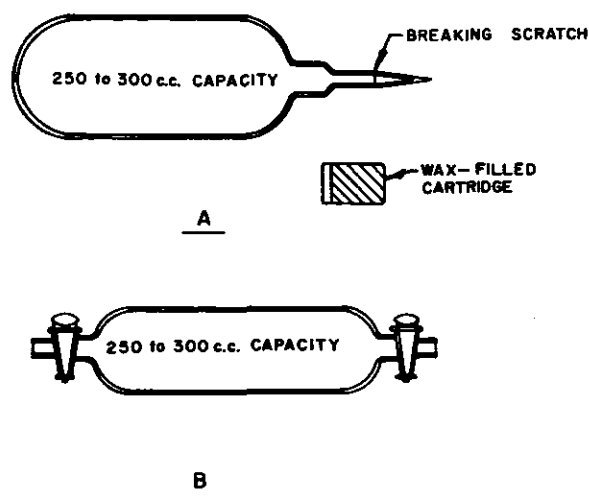
Grab samples are not limited to sampling gross amounts of gases or vapor. The introduction of highly sensitive and sophisticated instrumentation, including infrared spectrophotometry and gas chromatography, has extended the applications of grab sampling to low levels of contaminants.¹ In areas where the atmosphere remains constant the grab sample will be representative of the average as well as the momentary concentration of the components and thus it may truly represent an integrated equivalent. Where the atmospheric composition varies, peaks and valleys of contamination will be observed, and numerous samples must be taken to determine the average concentration of a specific component. The chief advantage of grab sampling methods is that their collection efficiency is normally considered to be 100 percent; there must, of course, be no losses due to leakage or chemical reaction preceding analysis.

Evacuated flasks are heavy-walled glass containers, usually of 250 or 300, but frequently of 500 or 1000, milliliter capacity (Figure 15-1A) from which 99.97 percent or more of the air has

been removed by a heavy duty vacuum pump. The internal pressure after the evacuation is practically zero. The neck is sealed by heating and drawing during the final stages of evacuation. These units are simple to use since no metering devices or pressure measurements are required. The pressure of the sample is taken as the barometric pressure reading at the site. After the sample has been collected by breaking the heat-sealed end, the flask is resealed with a ball of wax and transported to the laboratory for analysis.

A variation of this procedure with evacuated flasks is to add a liquid absorbent to the flask before it is evacuated and sealed to preserve the sample in a desirable form following collection.

Partially evacuated containers or vacuum bottles are prepared with a suction pump just before sampling is performed although frequently they are evacuated in the laboratory the day before a field visit. No attempt is made to bring the internal pressure to zero, but temperature readings and pressure measurements with a manometer are recorded after the evacuation, and again after the sample has been collected. This type of collector may include heavy-walled glass bottles, metal or heavy plastic containers with tubing connectors which are closed with screw clamps or stopcocks. The volume of air or gas taken into the bottle may be computed as described later in this chapter.



Sampling and Analysis of Mine Atmosphere, Miner's Circular 34. U.S. Dept. of Interior, 1948.

Figure 15-1. Grab Sample Bottles (A) Evacuated Flask (B) Gas or Liquid Displacement Type

Gas or liquid displacement collectors include 250-300 ml glass bulbs (Figure 15-1B) fitted with end tubes which can be closed with greased stopcocks or with rubber tubing and screw clamps. They are used widely in collecting samples containing O₂, CO₂, CO, N₂, and H₂ or other combustible gases for analysis by an Orsat or similar analyzer. Other devices operating on the liquid displacement principle include aspirator bottles

of various sizes which have exit openings at the bottom of the bottles through which the liquid is drained during sampling.

In applying the gas displacement technique, the samplers are purged conveniently with a bulb aspirator, hand pump, small vacuum pump or other suitable source of suction. Satisfactory purging is achieved by drawing a minimum of ten air changes of the test atmosphere through the gas collector.

The collectors mentioned in the gas displacement section can also be filled by liquid displacement. The most frequently employed liquid is water. In sampling, liquid in the container is drained or poured out slowly in the test area and replaced by air to be sampled. Application of this method is limited to those gases which are insoluble in and non-reactive with the displaced liquid. The solubility problem can be minimized by using mercury or water conditioned with the gas to be collected. Mercury, however, must be used with caution since it may create an exposure problem if handled carelessly.

Flexible plastic bags²⁻⁷ are used to collect air and breath samples containing organic and inorganic vapors and gases in concentrations ranging from parts per billion to more than 10 percent by volume in air and also to prepare known concentrations of gases and vapors for equipment calibration.⁸ The bags are easily inflated without stretching to their full volume using rubber squeeze bulbs or small hand pumps. They are available commercially in a variety of sizes, up to 9 cubic feet, but they may also be made in the laboratory. They are manufactured from several plastic materials including Saran, Scotchpak, Aluminized Scotchpak, Mylar, Aluminized Mylar, Teflon, Kel-F, Polyethylene and Polyester. The bag materials are from 1 to 5 mils in thickness and may be purchased in 100-foot or longer rolls of large sheets which may be cut to the desired size. Some, such as Mylar, may be sealed with a hot iron using a Mylar tape around the edges. Others, such as FEP Teflon, require high temperature and controlled pressure in sealing. Certain plastics, including Mylar and Scotchpak, may be laminated with aluminum which seals the pores and reduces the permeability of the inner walls to sample gases and the outer walls to moisture. Sampling ports may consist of a sampling tube molded into the fabricated bag and provided with a closing device or a clamp-on air valve. The 6- and 12-liter size are suitable for many industrial hygiene samples to be analyzed by infrared spectrophotometry using a 10-meter gas cell. Plastic bags have the advantages of being light, nonbreakable and inexpensive, and they permit the entire sample to be withdrawn without the difficulty associated with dilution by replacement air as is the case with rigid containers.

Plastic bags, however, must be used with caution since generalization of recovery characteristics of a given plastic cannot be extended to a broad range of gases and vapors. Important factors to be considered in using these collectors are: absorption and diffusion characteristics of the plastic material, concentration of the gas or vapor,

and reactive characteristics of the gas or vapor with moisture and with other constituents in the sample. A valuable summary of information sources on the storage properties of gases and vapors in plastic containers has been provided by Schuette⁹ and Nelson.¹⁰

The bags must be leak tested and preconditioned for 24 hours to the chemical vapors to be tested before they are used for sampling. Preconditioning consists of flushing the bag three to six times with the test gas, the number of refills depending on the nature of the bag material and the gas. In some cases it is recommended that the final refill remain in the bag overnight prior to the use of the bag for sampling. Such preconditioning is usually helpful in minimizing the rate of decay of a collected gas except for nitrogen dioxide. At the sampling site the air to be sampled is allowed to stand in the bag for several minutes, if possible, before removal and subsequent refilling of the bag with a sample. Once collected, the interval between sampling and analysis should be minimal.

Hypodermic syringes of 10- to 50-milliliter volume have also been used successfully for air sampling. These units are available usually in glass, but the disposable plastic type have also been used successfully. Ten milliliter Plastipak¹¹ syringes have been shown to have excellent retention properties for methane, hydrogen and other gases in normal mine air, but some loss of carbon dioxide was observed over a storage period of a week. The advantages of these units are cost, convenience and ease of use.

INTEGRATED SAMPLING

Integrated (or "continuous") sampling of the workroom atmosphere must be performed when the composition of the air is not uniform, the sensitivity requirements of the method of analysis necessitates sampling over a minimal (10-30 minutes) finite period, or when compliance or non-compliance with an 8-hour time-weighted average air standard must be established. Thus, the professional observations and judgment of the industrial hygienist are called upon in devising the strategy for the procurement of representative samples to meet the requirements of an environmental survey of the workplace.

Sampling Pumps

An integrated air sampling method requires a relatively constant source of suction as an air moving device. A vacuum line, if available, may be satisfactory. The most practical source, however, is an electrically powered pump or blower for prolonged periods of sampling. These come in various sizes and types and must be chosen for the sampling devices with which they will be used.

If electricity is not available or if flammable vapors present a fire hazard, aspirator bulbs, hand pumps, a portable unit operated by means of compressed gas (Freon; Unijet Sampler) or battery-operated pumps (activate outside the area to avoid a spark) are suitable for sampling at rates up to 2-3 liters per minute. For higher sampling requirements, ejectors using compressed air or a

water aspirator may be employed.

An air aspirator is usable where the pressure is constant. When compressed air or batteries are to be used as the driving force for a pump, the length of the sampling period is important in relation to the supply of compressed air or the life of the rechargeable battery. These units must not be allowed to run unattended and periodic checks on the air flow must be made.

Measurement of Air Flow

Air volume may be measured directly by means of an aspirator bottle, or by dry or wet test meters, but these units are used primarily in the laboratory for calibration purposes.

The common practice in the field is to sample for a measured period of time at a constant, known rate of air flow. Direct measurements are made with rate meters such as rotameters and orifice or capillary flowmeters. These units are small and convenient to use, but at very low rates of flow their accuracy decreases. The sampling period must be timed carefully with a stop watch.

Many pumps have inlet vacuum gauges or outlet pressure gauges attached. These gauges, upon proper calibration with a calibrated wet or dry gas meter, can be used to determine the flow-rate through the pump. The gauge may be calibrated in terms of cubic feet per minute or liters per minute. If the sample absorber does not have enough resistance to produce a pressure drop, a simple procedure is to introduce a capillary tube or other resistance into the train behind the sampling unit.

Sampling Trains

Samplers are always used in assembly with an air moving device (source of suction), and an air metering unit. These are the basic essentials. Frequently, however, the sampling train may consist of a filter, probe, absorber (or adsorber), flowmeter, flow regulator and air mover. The filter is included to remove any particulate matter that may interfere in the analysis. It should be ascertained that it does not also remove the gaseous contaminant of interest. The probe or sampling line is extended beyond the sampler to reach a desired location. It also must be checked to determine that it does not collect a portion of the sample. The meter which follows the sampler indicates the flow-rate of air passing through the system. The flow regulator controls the air flow. Finally at the end of the train the air mover provides the driving force.

Collection Efficiency of Samplers

Several methods of testing the efficiency of an absorbing, or adsorbing, device are available. One or more of these methods should be employed for periodic evaluation of individual units, in particular fritted bubblers whose porosities are subject to change from the effects of sampling corrosive atmospheric contaminants.

A recommended test system is a gas tight chamber or tank in which known concentrations of a given contaminant can be prepared. Absorbers are attached to sampling ports and operated under simulated field conditions to determine their collection efficiencies.

Frequently the relative efficiency of a single

absorber can be estimated by placing another in series with it. Any leakage is carried over into the second collector. The absence of any carry-over is not in itself an absolute indication of the efficiency of the test absorber since it may be possible that the contaminant is not stopped effectively by either absorber. Analysis of the two legs of a U-tube containing silica gel used in sampling a contaminant is a useful check on the collection efficiency of the first leg of the tube.

Another valuable technique is the operation of the test absorber in parallel or in series with a different type of collector having a known high collection efficiency (an absolute collector if one is available) for the contaminant of interest. By running the test absorber at different rates of flow the maximum permissible rate of flow for the device can be ascertained.

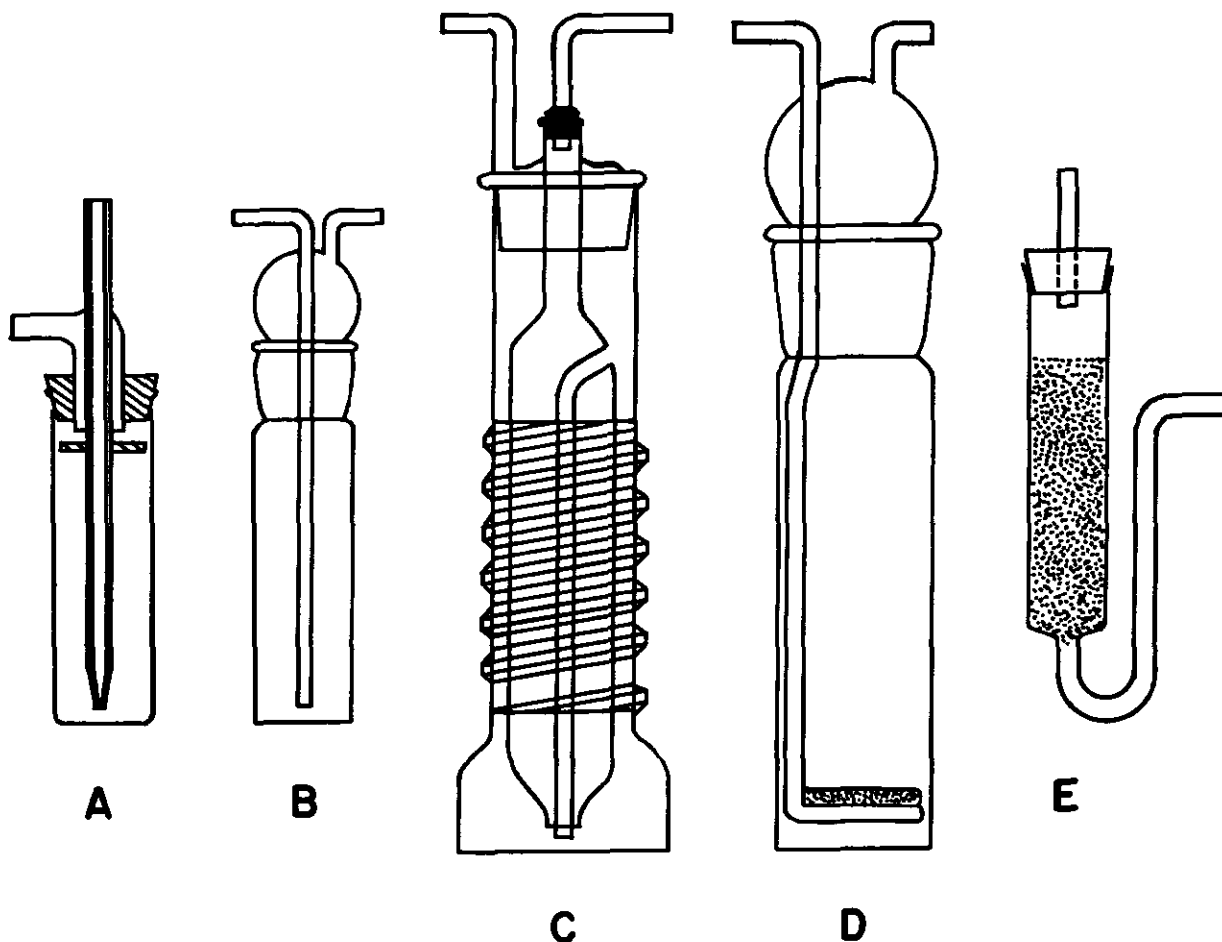
Discussion of Variable Factors Influencing Efficiency of Collection

A high collection efficiency is achieved when a chemically reactive sampling medium is used at a sufficiently slow rate to collect a contaminant with which it reacts to form a nonvolatile product. Such is the case in neutralization reactions of caustic scrubbing solutions with acid gases such as HF, HCl, SO₂, and nitrous fumes and the hydrolysis of toluene diisocyanate in Marcali Solution.¹² Other examples are given in Table 15-1 where collection efficiencies of 95 percent are reported generally for this type of sampling system. Long-term sampling may thus be conducted provided an excess of the collecting reagent is maintained.

Gases and vapors can also be collected satisfactorily in liquids that are not reactive if the contaminant is readily soluble in the medium. Thus, methanol and formaldehyde may be absorbed readily in water and esters in alcohol. The vapor pressure of these contaminants is lowered by the solvent effect of the absorbing liquid.

A discussion of the theoretical and practical aspects of absorbing vapors in non-reacting liquids is given by Elkins.¹³ It is emphasized that the variable which determines the efficiency of collection in a given system is the ratio of the volume of sampled air to the volume of the collecting liquid. The concentration of vapor in the air actually has no effect on the collection efficiency of non-reacting absorbing media. Other factors to be considered are: the degree of contact between the gas or vapor being sampled and the absorbent, duration of contact of the contaminant with the absorbent, rates of diffusion of gas and liquid phases, degree of solubility of the contaminant in the absorbent, and volatility of the contaminant.

The collection efficiency (the ratio of the amount of contaminant retained by the absorbing medium to that entering it) need not be 100 percent as long as it is known, constant and reproducible. The minimal acceptable collection performance in a sampling system is usually 90 percent, but higher efficiency is certainly desirable. When the efficiency falls below the acceptable minimum, sampling may be carried out at a lower rate, or at a reduced temperature by immersing



American Society for Testing and Materials: Tentative Methods of Sampling Atmospheres for Analyses of Gases and Vapors. Philadelphia, July 24, 1956.

Figure 15-2. Absorbers: A and B simple Gas Washing, C Helical Absorber, D Fritted Bubbler, E Glass Bead Column

the absorber in a cold bath to reduce the volatility of both the solute and solvent. It is often necessary to use two or more absorbers in series. Two bubblers in series have been shown to maintain a 95 percent efficiency of collection using water or isopropyl alcohol solvents with a sevenfold¹³ increase in the volume of sampled air (see Table 15-2). A fivefold bubbler system was proposed for the collection of organic chlorides.¹⁴

There are four basic types of absorbers employed for the collection of gases and vapors, classified as follows: simple gas washing bottles, spiral and helical absorbers, fritted bubblers and glass-bead columns. The function of these absorbers is to provide sufficient contact between the sampled air and the liquid surface to provide complete absorption of the gaseous contaminant. In general, the lower the sampling rate, the more complete is the absorption. See Figure 15-2 and Table 15-3.

Simple gas washing bottles include Drechsel types and standard Greenburg-Smith and midget impingers. In these devices the air is bubbled

through the liquid absorber without special effort to secure intimate mixing of air and liquid. The length of travel of the gas through the collecting medium is equivalent to the height of the absorbing liquid. These scrubbers are suitable for gases and vapors that are readily soluble in or react with the absorbing liquid. One or two units may be enough for efficient collection, but in some cases several in series may be required to attain the efficiency of a single fritted glass bubbler. Advantages of these devices are their simplicity in construction, ease of rinsing (for removing particulates), and the small volume of liquid required (with the exception of the Greenburg-Smith impinger).

The chief advantage of spiral and helical absorbers over simple gas washing bottles is that they provide a longer contact path between the sampled air and the absorbing solution. The sample is forced to travel a spiral or helical path through the liquid five to ten times that in the simpler units. Friedrichs and Milligan gas washing bottles are examples of this type of device.

TABLE 15-2

*The Effect of Two Bubblers in Series on Collection Efficiency of Non-Reactive Liquids

Vapor	Solvent	Maximum Air Volume in Liters for 95% Recovery	
		1 bubbler (10ml)	2 Bubblers (10 ml each)
Acetone	Water	0.8	5.4
Methanol	"	9.0	62.
n-Butanol	"	10.0	68.
Chloroform	Isopropanol	0.8	5.4
Carbon Tetrachloride	" "	0.5	3.4
Methyl Chloroform	" "	0.5	3.4
Trichloroethylene	" "	0.9	6.2

*Courtesy HB Elkins, Ph.D.

In fritted glass bubblers air passes through porous glass plates, and enters the liquid in the form of small bubbles. The size of the air bubbles depends on the nature of the liquid and the diameter of the orifices from which they emerge. Frits are classified as fine, coarse, or extra coarse, depending on the number of openings per unit area. The extra coarse frit is used when a more rapid flow is desired. The heavier froth generated by some liquids increases the time of contact of gas and liquid. These devices are more efficient collectors than the simple gas washing bottles and can be used for the majority of gases and vapors which are soluble in or react rapidly with the reagent. Rates of flow between 0.5 and 1.0 liter per minute are used. These absorbers are relatively sturdy, but the fritted glass is difficult to rinse out when used for contaminants which form a precipitate with the reagent, e.g., H_2S with $CdCl_2$. In

TABLE 15-3

Sampling and Absorbent Capacity of Absorbers

Type of Absorber	Absorbent Capacity (ml)	Sample Rate ml/min.
Simple gas washing bottles (Figure 15-2 A and B)	5-100	5-3000
Spiral and Helical (Figure 15-2 C)	10-100	40-500
Fritted Bubblers (Figure 15-2 D)	1-100	500-100,000
Glass-bead Column (Figure 15-2 E)	5-50	500-2000

ASTM Tentative Methods of Sampling Atmospheres for Analysis of Gases and Vapors. July 24, 1956, Philadelphia, Penna.

these cases a simple gas washing bottle should be used.

Packed glass-bead columns are used for special situations where a concentrated solution is needed. Glass pearl beads are wetted with the absorbing solution and provide a large surface area for the collection of a sample. It is of historical interest to note that the absorption of benzene and other aromatic hydrocarbon vapors in nitrating acid has been performed with this type of absorber.¹⁵ It is especially useful when a viscous liquid is required. The rate of sampling is low, 0.25 to 0.5 liter of air per minute.

When it is desired to collect insoluble or non-reactive vapors, an adsorption technique is frequently the method of choice. Activated charcoal and silica gel, 6 to 20 mesh, are common adsorbents. Esters, acetates and other soluble compounds are sampled regularly on these adsorbents. Solid adsorbents require less manipulative care than do liquid absorbents, can provide high collection efficiencies and, with improved adsorption tube design and a better definition of desorption requirements, are becoming increasingly popular in industrial hygiene surveys.

Activated charcoal is an excellent adsorbent for most vapors boiling above $0^{\circ}C$, moderately effective for low-boiling gaseous substances, between $-100^{\circ}C$ and $0^{\circ}C$, such as ammonia, formaldehyde, and hydrogen sulfide, particularly if the carbon bed is refrigerated, but a poor collector of hydrogen, nitrogen and gases having boiling points below $-150^{\circ}C$. Its retentivity for sorbed vapor is twice that of alumina and several times that of silica gel. Because of its non-polar characteristics, organic gases and vapors are adsorbed in preference to atmospheric moisture, and sampling can be performed for long periods of time.

Numerous investigators have been directing their efforts to the study of the optimal conditions for the sampling of organic solvent vapors by adsorption on activated charcoal and the subsequent desorption of the collected sample components for analysis in the laboratory. Fraust and Hermann have developed valuable breakthrough data on aliphatic acetates in their evaluation of the effects of mass flowrates and four separate mesh sizes of Pittsburgh Activated Carbon Company Type BPL activated carbon.¹⁶ Working with 4-6, 8-12, 16-20 and 30-40 mesh sizes and using 5-in., 5 mm sampling tubes containing 0.5 gm of activated carbon, these investigators have shown that, with the exception of the 4-6 mesh carbon, typical breakthrough curves consist of two segments: (a) a plateau region of almost constant efficiency and (b) an S-curve portion where the efficiency drops to zero with continued sampling. The 4-6 mesh carbon proved to be a relatively inefficient absorber as it showed no plateau except at the lowest mass flowrate of 0.002 mM ethyl acetate per minute. The other mesh sizes each showed a plateau of high-efficiency adsorption that was independent of mass flow until breakthrough time. The 8-12 mesh adsorbent provided a definite plateau at 96% efficiency but butyl acetate sampled at a mass rate of 0.0204 mM/min for a period of approximately 45 min. In the experimental

system used in this study, the 0.0204 mM/min flowrate was maintained by sampling a 500 ppm concentration of the ester at 1.0 liter/min. The time periods shown for the plateau regions with butyl acetate varied approximately from several minutes with a flowrate of 0.0409 mM/min to about 550 min at the lowest of the eight flowrates evaluated, i.e., 0.0020 mM/min.

The 16-20 and 30-40 mesh carbon each provided a plateau at 98% efficiency with amyl and butyl acetates separately. Again, the duration of the plateau varied with the mass flowrate; however, the sharp distinction between the plateau and S-curve sections should facilitate the selection of the upper limit of sampling time for anticipated concentrations of the esters.

Fraust and Hermann found that the times required for breakthrough and for the collection efficiency to drop to 50% are nearly inversely proportional to the mass flowrate expressed on a molar basis but that the adsorption process is not affected significantly by differences in the molecular weight. Other investigators have reported on the optimal conditions for sampling organic vapors in the atmosphere with activated charcoal followed by desorption with carbon disulfide and gas chromatographic analysis of the sample components.¹⁷⁻¹⁸ Their procedures are based upon the method of Otterson and Guy.¹⁹ Reid and Halpin¹⁷ obtained average recoveries of mostly 90-100% in sampling a test chamber containing known concentrations of halogenated and aromatic hydrocarbons using Darco 12-20 mesh activated charcoal in 0.6 gm quantities in a 5-in., 6-mm i.d. tube, followed by desorption with 3 ml carbon disulfide and gas chromatographic analysis of an aliquot portion of the resulting solution. The method was applied to concentrations of the separately vaporized compounds equivalent to one-half, one, and two times the respective threshold limit values. The sampling rate was 2 liters/min in tubes packed to a prescribed pressure drop.

White et al.¹⁸ have shown that the first two of four 1-in. sections of 180 mg each of activated charcoal supported in a 6-in., 4-mm i.d. tube adsorbed vapor concentrations of fourteen organic solvents completely at two times the TLV levels and that the overall recoveries were equivalent to those obtained by desorption of the corresponding liquid state of each compound with 1 ml of carbon disulfide. These investigators conducted experimental desorption studies with the single compounds and with multiple combinations of halogenated hydrocarbons, aromatic hydrocarbons, pyridine, ethanol, isooctane, 2-butanone and ethyl ether. They concluded that a mixture of seven or fourteen of the compounds evaluated did not affect significantly the desorption efficiency for any one of the substances. The sampling rates ranged 0.5-2 liters/min with no apparent effect on overall efficiency. The 1-in. sections of charcoal reportedly have a saturation limit of 28-30 mg of a single solvent and 28-45 mg of the total group of fourteen solvents. In the case of butyl acetate, for example, a saturation limit of 30 mg/10 liters of air sampled (3000 mg/m³) is more than four times the 1970 threshold limit value of 710 mg/m³ for

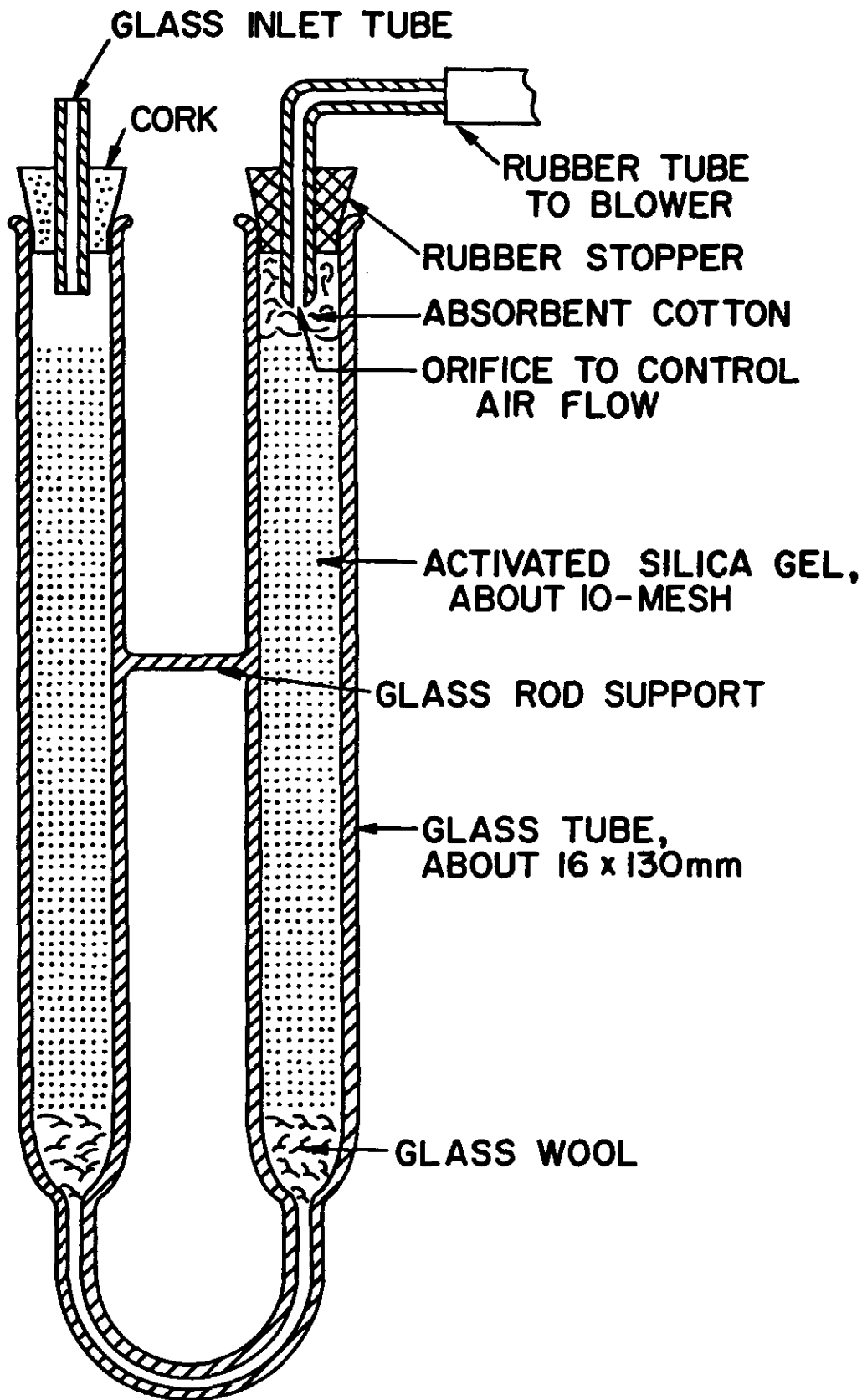
this ester, thus providing a comfortable margin of active adsorption sites when sampling at the TLV level.

Van Houten and Lee have reported their experiences in the use of 4-oz French Square bottles for the collection of atmospheric samples of solvent vapors for gas chromatographic analysis.¹ These bottles are filled by purging with an aspirator bulb fitted with two one-way valves. The bottles are capped quickly using a screw cap containing a 1/16 in. hole and provided with a set of four gaskets, one rubber and three Type 18 Saran, to prevent leakage of the collected sample. Aliquot portions of the sample are withdrawn through the port, using a calibrated syringe, and injected into the gas chromatograph for analysis. The authors have tested the effects of repetitive temperature changes over the 0-175°F range for a period of 7 days. The samples showed no appreciable loss from this treatment which was calculated to produce a pressure change equivalent to an altitude of 10,000 feet, considered as the effective altitude of the cargo compartment of commercial airliners. They concluded that the containers were suitable for shipping samples by air.

Silica gel (see U-tube, Figure 15-3) has been used widely as an adsorbent for gaseous contaminants in air samples. Because of its polar character it tends to attract polar or readily polarizable substances preferentially. The general order of decreasing polarizability or attraction is given as water, alcohols, aldehydes, ketones, esters, aromatic compounds, olefins and paraffins. (The polarity of chlorinated hydrocarbons is to a great extent determined by their structure.) Organic solvents are relatively non-polar in comparison with water, which is strongly adsorbed on silica gel; such compounds will be displaced by water in the entering air stream. Consequently, the volume of air samples collected under humid conditions may need to be restricted. Despite this limitation silica gel is a very useful adsorbent. It has been shown experimentally that, under conditions of 90 percent humidity, relatively heavy concentrations of benzene, toluene, and trichloroethylene could be adsorbed quantitatively from air passed through a tube charged with 10 grams of silica gel at the rate of 2.5 liters per minute for periods up to 20 minutes. Losses from the first to the second leg of a U-tube charged with silica gel was less when the humidity of the air was low.

Silica gel has been used for halogenated hydrocarbons²⁰⁻²² and nitrogen dioxide²³ and a wide range of organic solvents. The collection efficiency of the adsorbent can be increased by introducing a drying agent into the train.²⁴ Other factors that affect the collection efficiency include the volatility of vapor, mesh size of silica gel, rate of airflow and temperature.

Desorption of organic vapor is usually complete after the exposed gel has stood overnight in a correctly chosen solvent although, for many organic substances, the required elution period is much shorter. The lower molecular weight ketones are completely removed in an hour with water, benzene is eluted with isopropyl alcohol in about the same period whereas toluene and xylene



Elkins HB: The Chemistry of Industrial Toxicology, 2nd Edition. New York, John Wiley & Sons, p. 280.

Figure 15-3. Silica Gel Adsorber

are desorbed more slowly.

Other desorbing agents mentioned in the literature for silica gel are acetone and dimethylsulfoxide. The latter²¹ has been found particularly useful if the analysis is performed by gas chromatography. The retention time of this solvent is considerably greater than that of many common organic compounds. Poor recoveries were obtained with carbon disulfide; the addition of water after an initial contact period of two hours improved the desorption of toluene, xylene and certain halogenated hydrocarbons. Non-polar solvents are unsuitable for displacing vapors of aromatic hydrocarbons. Aliphatic hydrocarbons, for example, will not displace benzene.

The use of microcolumns of silica gel has been recommended for reducing bulkiness and cost of mailing sampling equipment.²⁵ Glass columns containing 500 mg of 42/80 mesh silica gel are prepared in three sections, and air is sampled at the low rate of 60 milliliters of air per minute. The presence of water and other polar substances may cause non-polar substances like benzene, cyclohexane, and toluene to migrate to a different section of the column. It was found necessary to analyze each section (by ultraviolet spectrophotometry) after elution with 5 milliliters of alcohol. Collection efficiency may be determined by the extent of migration of the adsorbate. Most laboratories now use gas chromatographic methods to analyze the eluates from solid adsorbents.

In condensation methods vapors or gases are separated from sampled air by passing the air through a coil immersed in a cooling medium, dry

ice and acetone, liquid air or liquid nitrogen. The device is not considered to be a portable field technique ordinarily. It may be necessary in certain cases to use this method where the gas or vapor may be altered by collecting in liquid or where it is difficult to collect by other techniques. Nitrogen dioxide and mercury vapor have been collected by this method prior to the development of more modern procedures. A feature of this method is that the contaminating material is obtained in a concentrated form. The partial pressure of the vapor can be measured when the system is brought back to room temperature.

ANALYSIS OF GASES AND VAPOR

A complete listing of methods of gas and vapor analysis is not intended, but a few of the commonly employed procedures are mentioned in Tables 15-1 and 15-4. Details of the analyses are found in the literature cited; additional procedures are found in the recommended publications listed in the reference section.

APPENDIX I

The direct measurement of the volume of an instantaneous (grab) sample of an atmosphere must be corrected to standard conditions of temperature and pressure in order to calculate the absolute quantity of matter which is to be determined. An understanding of the fundamental gas laws and their application is essential for this purpose. Examples of their applications are presented in this appendix.

TABLE 15-4
Gases and Vapors Collected on Solid Adsorbents and Their Analysis

Gas or Vapor	Sampler	Sorption Medium	Air Flow (L/m)	Adequate Sample (L)	Collection Efficiency	Analysis	Ref.
Wide range of organic vapors	Straight tube, 5 inches long, 6mm diameter	0.5 grams 12 x 20 mesh Activated Charcoal	0.1 to 1	2-10	*	Desorb with carbon disulfide, Inject into chromatograph	16-19
Wide range of organic vapors	U Tube	10 grams 8-16 mesh Silica Gel	3-5	25	*	Extract with alcohol, water, acetone for ultraviolet analysis or with dimethylsulfoxide for chromatography	20-25
Nitrogen dioxide	U Tube	10 grams 8-16 mesh Silica Gel	3-5	10-30	+90	Desorb with 50 ml sulfuric acid-peroxide solution *	13

* Depends on nature of solvent vapor, amount of adsorbent, sampling time and size of sample. For many organic vapors a sample of 25 liters will not leak into second arm of U tube.

* 1 ml concentrated Sulfuric Acid and 6 drops 30% hydrogen peroxide to 200 ml of water.

CALCULATIONS

Application of Gas Laws

At 0° C (273°K) and 760 mm pressure a gram molecular weight of any perfect gas will occupy a volume of 22.414 liters. If we ignore deviations from ideal behavior, oxygen of this volume would weigh 32 grams and nitrogen 28 grams, their molecular weights respectively. If there is a change in temperature and pressure the molar volumes of these gases will be altered. According to the laws of Boyle and Charles the change in molar volume will be inversely proportional to its pressure and directly proportional to its absolute temperature (°C+273).

In order for the actual measured volumes of gases and gas air mixtures to have meaning, they must be corrected to standard conditions of temperature and pressure (STP), 0° C (273°K) and 760 mm of mercury pressure.

From a consideration of the laws of Charles and Boyle is derived the equation:

$$V_{STP} = V_{\text{meas.}} \times \frac{P_{\text{bar.}}}{760} \times \frac{273}{273 + t^{\circ}C}$$

A correction for the presence of water vapor is made by subtracting the partial pressure of the water vapor in the air from the barometric pressure:

$$V_{STP} = V_{\text{meas.}} \times \frac{P_{\text{bar.}} - P_w}{760} \times \frac{273}{273 + t^{\circ}C}$$

t° C = temperature
at which
the sample
was taken.

If this formula is applied to a grab sample in a 12-liter volume bottle taken at 22°C at a barometric pressure of 760 mm, and a partial pressure of water vapor at 22°C of 19.8 mm, $V_{STP} = 10.8$ liters.

If an analysis of the grab sample showed it contained 5 mg of carbon tetrachloride, then:

$$\text{PPM} = \frac{\frac{\text{g}}{\text{MW}} \times 22.414}{V_{STP}} \times 10^6 = \frac{0.005 \times 22.414}{10.8} \times 10^6 = 67$$

MW = molecular weight of carbon tetrachloride
22.414 = molar volume (liters) of carbon tetrachloride at standard conditions of temperature and pressure (STP)

If the sample was taken in a partially evacuated flask, and a manometer reading showed that 365.1 mm of pressure remained in the flask, the formula for the corrected volume is:

$$V_{STP} = V_{\text{meas.}} \times \frac{P_{\text{bar.}} - P_w - P_p}{760} \times \frac{273}{273 + t^{\circ}C}$$

$$V_{STP} = 5.5$$

$$\text{PPM} = 132$$

Conversion Formulas

$$\text{mg per liter} \times 1000 = \text{mg per cubic meter}$$

$$\text{mg per liter} \times 28.32 = \text{mg per cubic foot}$$

$$\text{mg per cubic foot} \times 35.314 = \text{mg per cubic meter}$$

The common practice among industrial hygienists is to assume that air samples taken in normal factory air are at 25°C and 760 mm of mercury pressure. One gram molecular weight of a gas occupies 24.45 liters under these conditions. PPM (parts per million of a contaminant) may then be calculated from an air sample with the following simplified version of the expression given earlier:

$$\text{PPM} = \frac{24,450 \times \text{mg per liter}}{\text{molecular weight (contaminant)}} \times \frac{\text{mg per liter} = \text{mg of contaminant}}{\text{in one liter of air sample collected}}$$

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