AIR/PARTICULATE INSTRUMENTATION AND ANALYSIS

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PREFACE

Systems and instrumentation for measuring air properties are of interest and required by:

- those who do research or consult in the area of air pollution and its control as well as those interested in the basic properties of air and gases;
- engineers/technicians who work in plants that may generate pollution as a result of their processes; and
- those responsible for pollution regulation enforcement.

In these energy-conscious days engineers and scientists in industrial and utility plants must be aware of the pollution by-products their energy systems generate. This awareness embraces an understanding of not only the emissions themselves, but the ability to measure properties and constituencies of the emission. In existing plants and situations, direct measurements can be made. Accurate sampling and monitoring depend on the instrumentation, methods and apparatus used.

This volume presents a variety of analytical techniques and discussions by respective experts. Physical methods are focused for instrumentation and analysis of air/particulate systems and methodology. While there is no perfect measuring technique or no ideal measuring system, this does not mean that measuring systems are inadequate–quite the contrary. Highly sophisticated methods and equipment are applied to many measuring situations with great success, and progress is continually being made. In this book we focus on such measurement procedures and analyses.

Sincere thanks are due to the experts and specialists who contributed of their valuable time and knowledge to make this book possible.

Paul N. Cheremisinoff

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CHAPTER 1

PARTICLE MEASUREMENT TECHNIQUES

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INTRODUCTION

Techniques for measuring particle size and size distribution are numerous and are based on a variety of physical phenomena. This chapter reviews some of the measurement areas most applicable to the needs and potential requirements of industry.

Particle size distributions help determine such quantities as combustion efficiencies in sprayed fuels, flow characteristics of powdered and granular materials, the probability of a dust explosion in a dusty atmosphere, and process monitoring needs in latex manufacture to prevent filter clogging. Also, measurement of dust size distribution and concentration in working environments is required for personnel safety. A dust particulate size less than 5 μm is considered respirable.

Measurement techniques reviewed in this chapter include: sedimentation sieving, microscopy, the Coulter Counter, photography, laser shadowgraphy, holography, light scattering and hydrodynamic chromatography.

It can be concluded from the chapter that no instrument or type measurement technique is completely satisfactory as a universal method for particulate studies. Certainly, any endeavor in the particulate measurement area should begin with a thorough investigation of the nature of the potential applications.

The objectives of this chapter are (1) to review the various particle size environments (e.g., aerosols and particles in solution) and the techniques available for measuring particle sizes; and (2) to comment on the universality of each technique.

Before dealing with techniques of particle sizing, sizes of particles that may be encountered will be discussed. The definition of "particle" is a discrete portion of matter ranging, for our purposes, from atoms and molecules to gravel. In esoteric scientific circles, however, persons may be searching for methods of defining size and then attempting to measure sizes of the myriad elementary particles that make up neutrons, protons and electrons, the constituents of atoms. Astronomers and astrophysicists, however, might well be trying to measure the size of a distant star or galaxy—"particles" of the universe.

This discussion will be limited to techniques used in measuring particles from 0.01-0.1 μm (micrometer or micron) to the 1-cm particle diameter (Table I) [1]. Note that when particle diameter is given, the number is ambiguous for shapes other than spherical particles. For irregularly shaped particles, the "particle diameter" can be defined as the average linear measure of a projection of the particle. For large numbers of particles, and assuming random orientation of the particles, the resulting number is statistically acceptable. The use for which the measurements are intended should be considered before defining "particle size."

Particles studied using the techniques described herein are contained in a powder, a slurry, a stable emulsion or an aerosol (sprays included) [2]. Some techniques apply to most of the environments in which particles are found, but most schemes are applicable to only one of the classes.

Methods of measuring particle surface area and pore sizes will not be reviewed in this chapter. The techniques and analyses differ enough from the particle size methods to require a separate study.

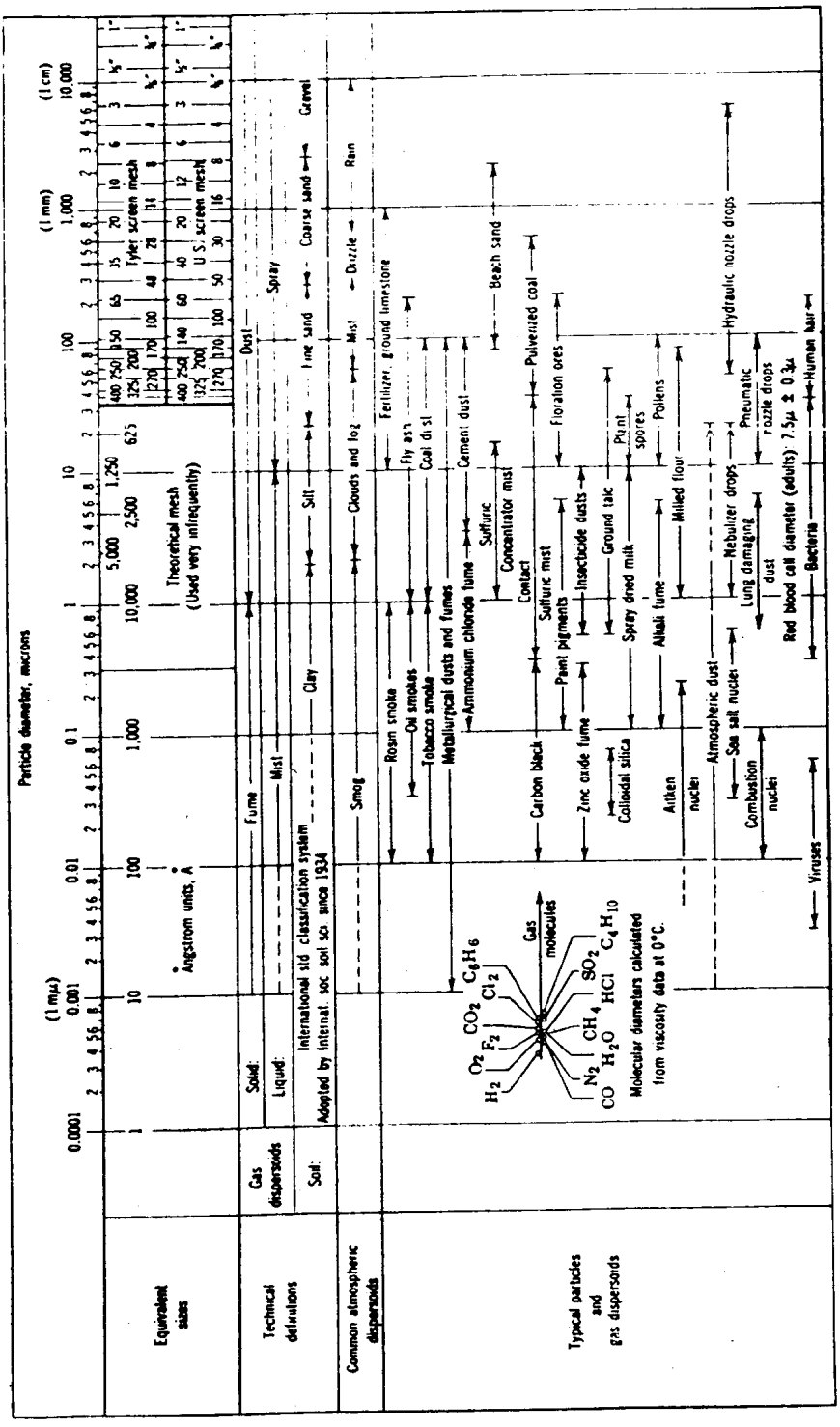
DISCUSSION

In this section, the older sizing methods [2-4] and the latest developments in particle size measurements will be reviewed. Also, the applicability of the techniques to the various particle environments will be discussed. The particle environment classifications are powders, slurries, stable emulsions and aerosols.

Sedimentation

A particle moving in a viscous medium experiences an opposing force proportional to its size and speed (Stokes law). One obvious driving force for the

Table I. Size Range of Typical Particles and Gas Dispersoids



particle (or particles) is the earth's gravitational field. The magnitude of the gravitational force, F_g, is

$$F_g = V\rho_p g \tag{1}$$

where ρ_p is the density of the particle, V is the volume of the particle and g is the gravitational acceleration. Actually, the particle will be in a surrounding medium, density ρ_m, so that the buoyant force must be taken into account. Hence, we have the driving force,

$$F_g = V(\rho_p - \rho_m)g \tag{2}$$

To increase the driving force, one can take advantage of centrifugal acceleration, which can be varied and is dependent on angular speed and distance from the axis of rotation. The magnitude of angular acceleration, a_c, is

$$a_c = \omega^2 R \tag{3}$$

where ω is the angular speed, $(d\theta/dt)$, of the particle and surrounding medium, and R is the radial position of the particle. The driving force for the centrifugal acceleration is

$$F_c = V(\rho_p - \rho_m)\omega^2 R \tag{4}$$

so the centrifugal driving force can be larger than the gravitational driving force for $\omega^2 R > g$. In some cases, as we will see later, the larger force will enable the study of very small particles and of stable emulsions to be performed.

From Equations 2 and 4 it appears that the particles would accelerate indefinitely; however, there is an opposing force exerted by the surrounding viscous medium. A simplified description of the opposing force, F_s, was given by Stokes:

$$F_s = -3\pi\eta\nu d \tag{5}$$

where η is the shear viscosity of the fluid, ν is the speed of the particle and d is the diameter of the particle (assumed to be a sphere). Equation 5 holds true for spherical particles that are large compared to the particle size of the surrounding medium and for low particle speed. As the particle approaches the size of the surrounding medium particle size, slippage can occur in the interstitial regions between particles of the surrounding medium.

Infrequently, the particles being examined are spherical. For irregularly shaped particles, where

$$\frac{\text{maximum diameter}}{\text{minimum diameter}} \leq 4 \tag{6}$$

all possible particle diameters can be averaged to yield an average diameter, $\bar{d}$. Stokes law can be rewritten for nonspherical particles [5]:

$$F_{NS} = 3\pi\eta\nu\bar{d} \tag{7}$$

When the net force on the particle is zero, the particle will maintain a terminal velocity. For the gravitational driving force, the terminal velocity is achieved when

$$F_g + F_{NS} = 0 \tag{8}$$

From Equations 2 and 7 we have

$$V(\rho_p - \rho_m)g - 3\pi\eta\nu\bar{d} = 0 \tag{9}$$

The particle volume, V, can be written as

$$V = \frac{\alpha\pi\bar{d}}{6} \tag{10}$$

where $\alpha = 1$ for a sphere. Combining Equations 9 and 10 and solving for the average particle diameter:

$$\bar{d}^2 = \frac{18\,\eta\nu}{\alpha(\rho_p - \rho_m)g}$$

or

$$\bar{d} = \left(\frac{18\,\eta\nu}{\alpha(\rho_p - \rho_m)g}\right)^{1/2} \tag{11}$$

Consider examples of particles of density 2.0 g/cm^3 settling in water at a temperature of 25°C. Quantities of interest to be calculated are the distance traveled by the particle before reaching terminal velocity and the terminal short distance; then the falling distance can be measured as a function of time to determine the particle diameter. To solve for the falling distance prior to reaching terminal velocity, one must set

$$F_g + F_{NS} = ma \tag{12}$$

which is, in terms of distance, s,

$$\frac{\pi \bar{d}}{6}(\rho_p - \rho_m)\, g - 3\pi\eta\bar{d}\,\frac{ds}{dt} = \frac{6\rho_p}{\pi\bar{d}^3}\,\frac{d^2s}{dt^2} \tag{13}$$

for a spherical particle. Equation 13 is a differential equation, which can be solved for distance, s, as a function of time.

Table II is the result of an example calculation performed by Irani and Callis [2]. As can be seen from the table, there is a narrow range of particle diameters over which gravitational sedimentation can be used.

To determine particle sizes of very small particles, the centrifuge technique must be used. Also, if ρ_p is approximately equal to ρ_m (stable emulsions), a large driving force must be used. In the centrifuge technique, the equations are changed by replacing the gravitational acceleration, g, by the centrifugal accelearation, $\omega^2 R$. Hence, by increasing the angular speed, the driving force can be increased.

It has been shown that different size particles (assuming all have the same density) can be separated by the gravitational or centrifugal sedimentation

Table II. Rate of Fall in Water at 25°C for Particles Having a Specific Gravity of 2

Size (μ)	Approximate Distance Traveled Prior to Reaching Terminal Velocity (cm)	Approximate Terminal Velocity (cm/sec)
2000	1.2×10^{2}	240
200	1.2×10^{-2}	2.4
20	1.2×10^{-6}	2.4×10^{-2}
2	1.2×10^{-10}	2.4×10^{-4}
0.2	1.2×10^{-14}	2.4×10^{-6}
0.02	1.2×10^{-18}	2.4×10^{-8}

techniques. Once the particles have been grouped into sizes, the problem exists of measuring the concentration of the various size particles. There are numerous methods of measuring the particle concentration in liquids at a given height as a function of time. Included in these methods are drivers (small modules of known density), a hydrometer, a manometer, light scattering to measure the change in turbidity with particle size, neutron activation analysis and X-ray transmission. Of course, any one of the measurement methods is not usable for all types of particulate composition. In general, the concentration measuring technique must be chosen based on the nature of the particle material to be studied. For example, one company that uses the classical sedimentation approach in its instrumentation is Micometrics Instrument Corporation.*

The use of sedimentation by gravitational or centrifugal driving forces historically has been a very useful technique for particle sizing. However, difficulties do occur for rather broad particle size distributions. The same problem arises, however, for other techniques described later. Wallace and DeCann [6] explain their hybrid technique of combining ultracentrifugation with angular light scattering to measure size distributions of collodial suspensions of a polydisperse nature or a multimodal distribution. Simply, the technique uses ultracentrifugation to fractionate the distribution. Then, portions of the separation are examined with angular light scattering to measure particle size. In this manner, the distribution of the polydisperse or multimodal suspension can be constructed. The angular light scattering technique is discussed in a later section.

The sedimentation technique has been used to determine particle size distribution of powders, slurries and stable emulsions. Powders, of course, must be placed in a suitable liquid for study. When broad or multimodal size distributions are present, there are difficulties with the classical technique of sedimentation. Hybrid techniques then may be used to perform the measurement.

Sieving

Sieving, perhaps the simplest technique of particle size measurement, is a way of coarsely measuring particle size distribution by subjecting a group of particles to a fixed opening and measuring the particles that remain in the container. A series of different opening sizes can be used to further determine the size distribution.

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*Micrometrics Instrument Corporation, 800 Groshen Springs Road, Norcross, GA 30071.

A wide range of standard opening sizes are being used. The United States Sieve Series ranges from Mesh No. 3 1/2, 5.66 mm opening, to Mesh No. 4000, 0.037 mm or 37 μm opening [2]. Mesh sizes are related to Mesh No. 18, having an opening of 1.00 mm. The Tyler Standard Sieve series, however, is based on the English System inch. The Tyler Series ranges from Mesh No. 3 1/2, opening 5.613 mm, to Mesh No. 400, opening 0.038 mm, or 38 μm. For a given mesh number, the openings in each series are approximately the same. The micromesh construction technique of etching has lowered the usable mesh size to 20 μm with conventional mechanical sieve agitation [7].

Particles in powders, slurries and stable emulsions can be measured with the sieve method. However, wet sieving does present the added problem of having to dry the material that remains on the sieve before weighing. Also, for many applications, the 20-μm lower limit is too large for the study. However, sieving remains the most widely used particle size measuring technique.

Sieving technology is progressing in the areas of microsieve construction and of sample agitation. Figure 1 shows a schematic of a Sonic Sifter manufactured by ATM Corporation, Sonic Sifter Division, Milwaukee, Wisconsin. The sifter can handle a particle size range from 850 μm to a lower limit of 5 μm. As can be seen in Figure 1, the upper diaphragm oscillates (like a loudspeaker), which then causes oscillation of the sample via air movement and, hence, agitation. The amplitude of the diaphragm oscillation can vary according to the density, particle size and volume of sample material. The sonic agitation, as claimed by the manufacturer, enables the measurements of particles as small as 5 μm to be performed quickly.

Microscopy

Microscopy has a nominal size measurement range of 0.001 to 100 μm [2]. Several types of microscopes, however, are needed to span the range. The lower end of the range is covered by the electron microscope, 0.001-5 μm, and darkfield microscopy or ultramicroscopy, 0.01-0.2 μm and white light microscopy, 0.4-100 μm. Different types of microscopes are required because the lower resolution limit of an optical type device is a direct function of the wavelength of the particle in irradiating the sample; that is, electrons have a shorter wavelength than visible or ultraviolet light.

For cases in which the actual shape of a particle is of interest, microscopy yields direct observation of the particle. Hence, the shape can be qualitatively noted and the average size determined.

Difficulties associated with microscopic measurements of particle distribution include sample preparation and the actual counting and sizing of the

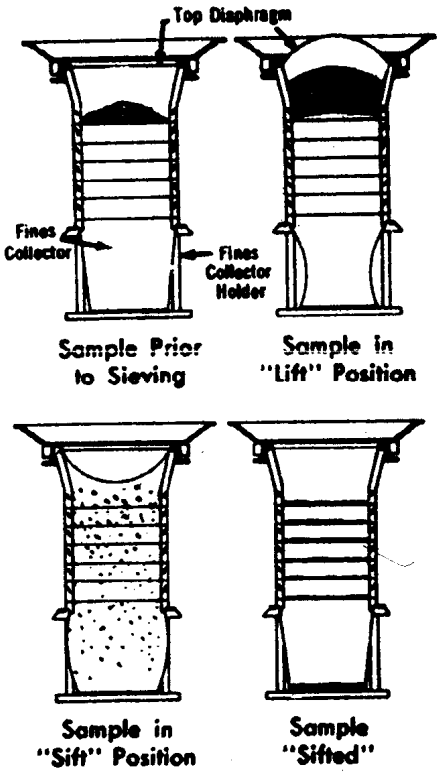

Figure 1. Schematic diagram of sieving by sonic agitation. (Apparatus manufactured by ATM Corporation, Sonic Sifter Division.)

magnified particles. Slide preparation is critical in that one must be assured that the resulting slide is representative of the particle distribution. Once a procedure for representative slide preparation has been established, the size distribution is then measured by actually scanning the slide, measuring and counting individual particles. There are, at considerable cost, computerized counting systems available to perform the size measuring, shape and counting. One such system, the Quantimet 720 Image Analysing Computer, is manufactured by Image Analysing Computers, Inc.* The manufacturer claims that 4000 particles per minute can be identified, counted, measured and classified by computerized microscope.

*Image Analysing Computers, Inc., 40 Robert Pitt Drive, Monsey, NY 10952.

Particles contained in a powder, slurry, stable emulsion or aerosol can be measured with microscopy. In aerosols, though, there is the potential problem of disturbing the aerosol geometry by the presence of a light microscope. A microscope has a very short focal length and must be positioned quite close to the sample. If the measurement of the aerosol involves a determination of a spatial size distribution, other techniques, such as photography or laser shadowgraphy, should then be considered.

Coulter Counter®*

The Coulter Counter technique is based on a change in conductivity or resistance between two electrodes immersed in an electrically conductive liquid. Figure 2 is a schematic diagram of the Coulter Counter [8]. Referring to Figure 2, note that the electric current flowing between electrodes A and

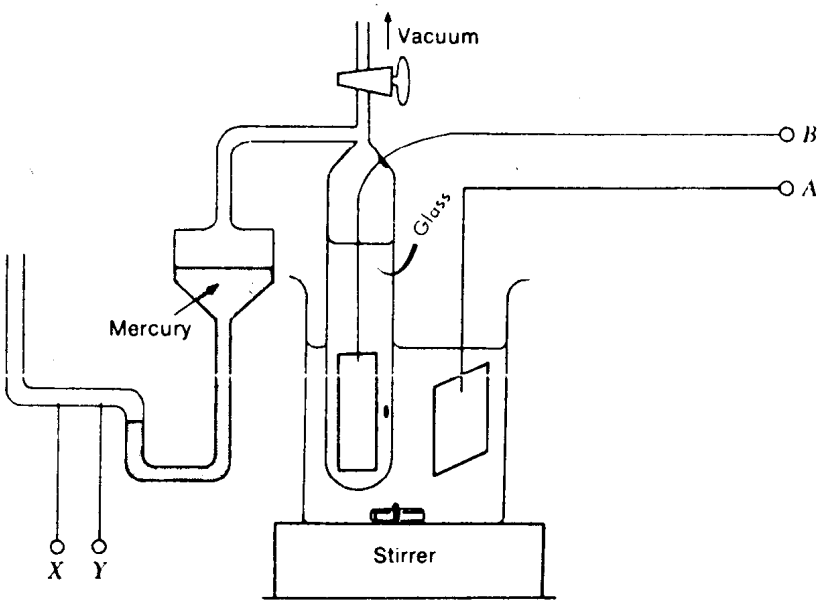

Figure 2. Schematic diagram of a Coulter Counter.

*Registered trademark of Coulter Electronics, Inc., 590 West 20th Street, Hialeah, FL 33010.

B must pass through a small hole. Now suppose that a particle passes through the hole. The particle displaces the conducting solution, increasing the resistance between the electrode. A different size (volume) particle correspondingly displaces a different amount of solution and causes a resistance change proportional to the amount of solution displaced. Since the resistance change is proportional to average particle size, a pulse height analyzer can be used to record and classify the particles passing through the hole. A time scan can be performed by evacuating the air above the solution in the glass container. The mercury column passing through electrodes X and Y would provide scan start and stop signals.

There have been efforts to determine shapes of particles with the Coulter technique [9]. These studies of shape determination are based on the fact that particles may change orientation as they pass through the hole in the Coulter system. As the particles tumble, a slight change in resistance will be noticed, and the signature of the resistance pulse could correlate with the shape of the particle. Further, Spraker et al. [9] give an explanation of the 30% difference of a size distribution of paper mulberry pollen particles of measurements by the Coulter Counter and a scanning electron microscope. The authors explain that, assuming absorption of the conducting medium by the pollen particles, they obtain agreement with the theoretical approach of Maxwell's equation for the resistivity of conducting spheres in suspension.

The main difficulty with the Coulter Counter method is the requirement that the particles to be measured be contained in a conducting solution. It is possible that the medium could interact with the particles or solvate them. For particles with chemically inert surfaces, there have been no particle-solution interactions measured.

The size range of particle measurement by the Coulter Counter is from 0.5 to 500 μm, as reported by the manufacturer. However, no satisfactory data have been reported below 5 μm and above 100 μm [2].

Photography for Aerosol Studies

As mentioned in the section on microscopy, p. 8, the difficulty in using a microscope for aerosol particle size studies is the short focal length of the microscope. To study the particle size in a flowing aerosol, the microscope must be placed very near or within the particle flow field. The presence of the microscope perturbs the aerosol pattern and experimental error is introduced. To circumvent the short focal length problem, studies with a conventional camera have been conducted by the author.