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# Review
# The generation and measurement of aerosols

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Aerosols are of extreme importance to many branches of science and technology although this is seldom realized by non-specialists. The disperse phase of an aerosol may consist of virtually any known material and so includes liquids, pure and unadulterated, as well as solids of simple composition and regular shape in one extreme to complex materials which may be radioactive, electrically charged and of complex shape in the other extreme.

The basic characteristics and some of the most important methods of generating aerosols are reviewed. The difficulties that arise in attempting to produce standard aerosols are indicated. In considering measurements on aerosols the difficultues in collecting representative samples are outlined. Diagnostic methods which do not perturb the aerosol such as photographic and holographic techniques as well as light interaction methods are considered in some detail.

## 1. Introduction

The usual implication of the word aerosol is a spray of liquid droplets of such substances as paints and perfumes. The word was first used by Donnan [1] towards the end of the first world war to describe fine aerial dispersions and smokes of the arsenical type. Schmauss apparently, quite independently, used the word in 1920 [1]. An aerosol is a two-phase system in which the dispersion medium is a gas, usually air, and the disperse phase is a liquid or a solid. Particle size is sufficiently large to enable optical methods to be used in diagnosis but not large enough for particles to rapidly settle out of the system. Brownian motion of aerosol particles generally occurs. The system is, therefore, relatively stable and has a near counterpart in the water-colloidal suspension known as the hydrosol. In practice, the size of aerosol particles usually lies in the range 0.1 to 50 μm, although there are many instances of systems of particles outside this range, being described as aerosols. In mentioning particle size it is important to realize that most aerosols consist of particles with a distribution of size and these aerosols are said to be polydisperse. The size distribution is rarely Gaussian but often has a logarithmic form. In some instances, systems occur in which particle size is fairly constant within narrow limits, and these systems are said to be monodisperse.

In classifying a system as monodisperse it is desirable to specify the tolerance on particle size, and this may conveniently be done by stating the relative standard deviation, $\alpha$, as the ratio of the standard deviation of the particle radii, to the mean radius. With this definition, aerosols for which $\alpha \leqslant 0.2$ may be considered to be monodisperse. Some of the best examples of naturally occurring monodisperse systems are microbiological, in which the disperse phase consists of spores or pollen. A particularly well-known spore, which is widely used as a reference, is the lycopodium spore which has a mean radius of 15 μm and $\alpha = 0.10$.

There are several common disperse systems which may be properly described as aerosols but which are known by other more familiar names. Let us consider, for example, smokes, mists and fogs. Smokes generally consist of solid, irregular particles in the size range from below 0.1 μm to 5 μm and, although settling slowly occurs, the degree of stability of a smoke is such that it is classified as an aerosol. The typical blue colour of cigarette smoke is due to scattering of visible radiation by the solid particles of about 0.1 µm in diameter. The disperse phase of a mist consists of droplets formed by condensation from the vapour phase, or by atomization of a liquid. The droplets are larger than in a smoke and range up to about 10 µm in diameter. Droplet density is relatively low compared with a fog, but differentiation between mists and fogs is sometimes difficult, as the line of demarcation is ill defined. A definition based upon range of visibility is often used to distinguish between a mist and a fog.

To describe the amount of literature on aerosols as extensive is an understatement. The citing of a few instances in which aerosols play a major role should suffice to illustrate this point. It will be appreciated that in such a wide-ranging, interdisciplinary subject there are many specialized aerosol generation techniques. No attempt has been made to review all of these. Instead, only the most widely used methods are considered.

Atmospheric pollution and control of our environment are emotive topics in which aerosols, in various forms, play a central role. Pollution by vehicle exhausts, industrial plant and aircraft can be understood by studying the aerosol formation processes at the sources of pollution. In engines, aerosols are produced by the atomization of fuel, and the characteristics of the fuel aerosol greatly influence the content and character of the exhausted aerosol with which we are so familiar, especially when close to an incorrectly adjusted diesel vehicle. Although we endeavour to cleanse our environment by removing atmospheric pollution we also try to exert active control when we precipitate rainfall by the release of aerosols of silver iodide and other substances. Studies of radioactive fall-out from nuclear explosions are studies of large-scale aerosols. Aerosol spraying of paint, in either liquid or solid particle form, is now well established in industry. Electrification of a paint aerosol leads to considerable improvements in the painting process. Crop spraying is another similar application where electrification may be of considerable benefit. Electrified aerosols are directly responsible for recent catastrophic explosions which have occurred during tank washing of large oil tankers. Similar problems occur in coal pulverization mills and flour mills. Finally, we might mention two interesting aircraft problems. Dumping of fuel from aircraft during an emergency is not uncommon and the fuel is dispersed by aerodynamic forces into an aerosol soon after ejection. Farmers are happy to spray their crops with insecticides but not quite so pleased to have them sprayed with aviation fuel! Recently, work has been reported which aims at preventing aircraft fuel from disrupting into an aerosol spray during a high-impact accident. The fuel, therefore, requires to have anti-dispersal properties yet it must still be atomized in the engines. It remains to be seen whether or not these two conflicting requirements can be reconciled.

## 2. Aerosol formation

Aerosols are formed in one of the two following ways:

1. physical dispersion of a liquid or a solid;
2. condensation.

In considering physical dispersion of a liquid we include aerodynamic, hydrodynamic, centrifugal, ultrasonic and electrostatic methods. The liquid may be pure or it may be a suspension or a solution. A well-known dispersion method, for solids, is the aerodynamic dispersion of powders. Also, there are some explosive techniques which, produce aerosols directly from the unpowdered solid phase, but usually only as a by-product.

Condensation methods of aerosol formation rely upon precipitation of droplets from a supersaturated vapour/gas mixture. Precipitation may be spontaneous or nucleation centres, such as ions, may be provided. Other methods depend on cooling a hot vapour/gas mixture either in a heat exchanger or by mixing with a cold gas. One other "condensation" method uses chemical reaction in the gas phase to generate the disperse phase.

A summary of aerosol generation methods is given in Fig. 1. The more important of these methods will be considered.

## 3. Aerosol formation by dispersion

In order to disperse bulk liquid to form an aerosol, energy must be supplied to account for the increased surface area, and thus surface energy, of the disperse phase over that of the initial bulk liquid. The manner in which the transition from bulk to disperse phase occurs is exceedingly complex, but invariably either filaments or sheets of liquid initially form and then collapse into droplets. In some processes, filaments and sheets are both formed and this is beautifully illustrated by the photographs, taken

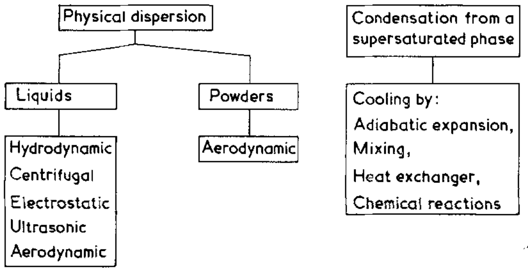

*Figure 1* Aerosol generation methods.

by W. R. Lane, of a drop disrupting by aerodynamic forces as shown in Fig. 2. The bubble-like sheet of liquid from the centre of the drop first collapses into very fine droplets, followed by the relatively thick rim of liquid collapsing into larger droplets.

### 3.1. Aerodynamic dispersion

The production of liquid-droplet aerosols by aerodynamic atomizers is well known because of such common applications as paint and insecticide spraying. These atomizers, in their simplest form, operate by blasting air across the top of a pipe so that the pressure within the pipe is reduced below atmospheric. Liquid is sucked up from the bottom of the pipe and is atomized at the top by the air blast. The disruption processes at the top of the tube are complex with liquid being torn off in ligaments and sheets which collapse into droplets. Dombrowski *et al.* [2, 3] carried out a thorough photographic investigation into the disruption of liquid films.

Aerosols produced by gas blasts are invariably polydisperse. An empirical expression for the size distribution of droplets in mists produced by small air-blast atomizers, was found by Nukiyama and Tanasawa [4] and is

$$\frac{\mathrm{d}n}{\mathrm{d}x} = ax^{\mathrm{p}} \exp\left(-bx^{\mathrm{q}}\right)$$

where d$n$ is the number of droplets in the size range $x \pm (\delta x/2)$ and $a$, $b$, $p$, and $q$ are experimentally determined constants. Nukiyama and Tanasawa's work was done using subsonic gas flows. Bitron [5] extended the experiments to supersonic flows and showed that the empirical relationships determined by Nukiyama and Tanasawa remain valid.

Considerable refinements in air-blast atomizer design are possible if baffles are used to separate out larger, generally unwanted, droplets from the aerosol. A baffled arrangement was first described in 1932 at a meeting of the British Medical Association by Collison [6] and this "inhaler" now bears his name and is the basis of a British Standard (1955). Fig. 3 shows schematically the British Standard Apparatus. The liquid reservoir is relatively large (several hundred ml) so that evaporation from volatile solution is

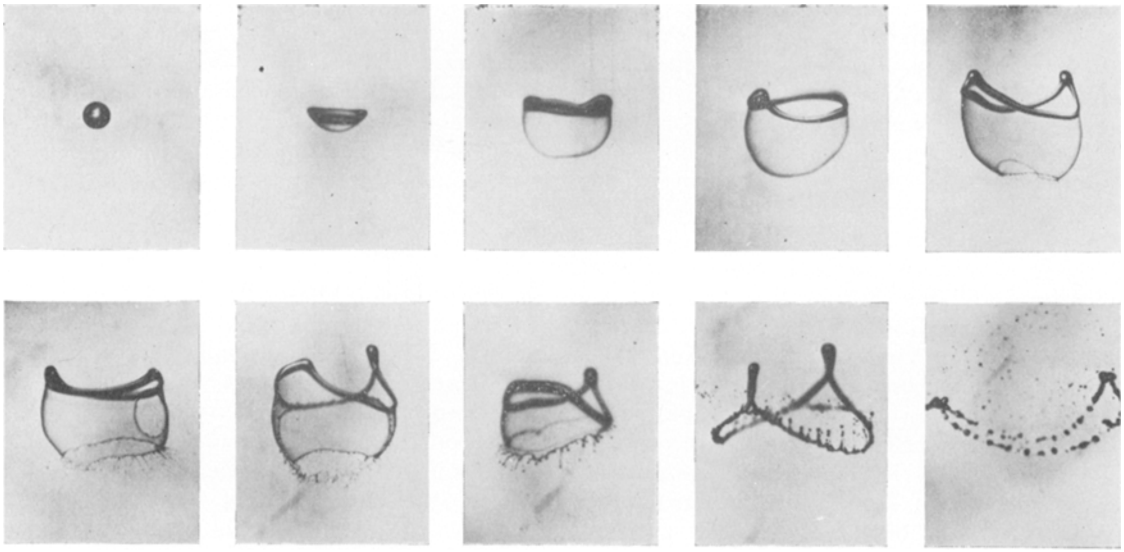

*Figure 2* Break-up of a water drop in a steady airflow. Drop diameter is 2.6 mm, air velocity is 22.5 m sec$^{-1}$ (Reproduced by permission of the Controller of Her Majesty's Stationery Office.)

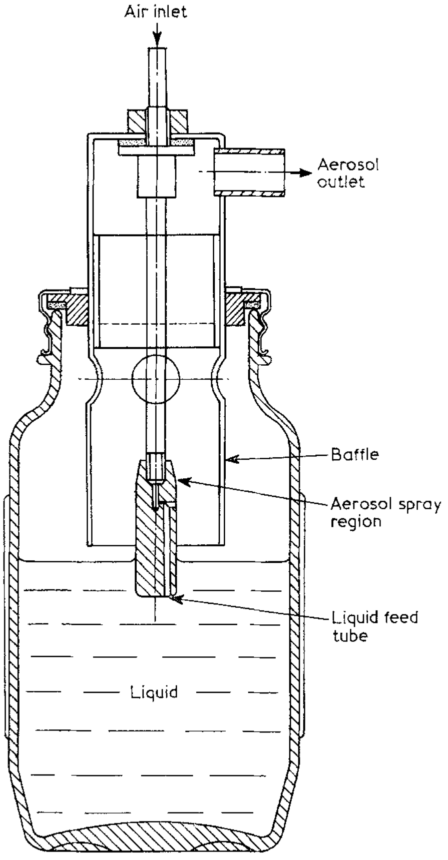

*Figure 3* The Collison nebuliser.

relatively unimportant and negligible changes in concentration of the liquid occur. Very often, especially when dealing with toxic or precious liquids, it is undesirable to have a large fluid reservoir, and Druett [7] modified the apparatus by arranging to have a low-volume bulge in the bottom of the reservoir into which dipped the end of the atomizer tube. Also, the main reservoir diameter was reduced, so that the walls were closer to the atomizer head and behaved as a baffle. May [8] gives a detailed description of Collison atomizers with information on operating characteristics, including air and liquid consumption, aerosol output and droplet size distribution.

Collison atomizers operate effectively from an air-pressure line delivering air in the pressure range 15 to 50 psi*. The baffles intercept the majority of droplets having diameters greater than about 10 µm although a few large droplets of the maximum size that the upflow of air in the apparatus can support, are emitted. With water, a few drops with diameters up to about 55 µm are detectable. The baffles intercept the greater portion of the aerosol flow from the atomizer head, and May states that with water as much as 99.92% of the atomized liquid is refluxed back into the reservoir. Baffling is believed to be an interceptive process with very little shatter of droplets taking place.

In testing industrial filters and respirators, an aerosol of solid particles with a standard size distribution is required. One method of producing such an aerosol to a British Standard Specification is to use a Collison atomizer to disperse a 5% by weight solution of sodium chloride, which is then allowed to evaporate to produce an aerosol of sodium chloride crystals of mean size about 0.6 µm. Fig. 4 shows an electron microphotograph of salt particles formed in this way. This photograph was kindly supplied by the Physics Division of the Chemical Defence Establishment, Porton. Sodium spectral-line measurements on either side of a filter enable an accurate assessment of filter effectiveness to be made.

The aerodynamic dispersion of powders is well known in the paint industry where surfaces are sprayed with powdered paint and then heat-treated to produce a tightly-bonded painted surface. Initial adhesion to the sprayed surface may be electrostatic, or due to molecular forces. Many of the industrial powder-dispersion systems are simple and consist of a hopper containing the powder, which feeds directly into an air-blast region. The hopper usually has to be rapped periodically or vibrated to ensure continuity of feed.

Other industrial systems use fluidized beds of powder, sometimes electrostatically charged, and it is possible to coat articles on a production-line basis. Steel cables, for instance, have been drawn through such a system and coated with protective wax at speeds of 180 ft min$^{-1}$.†

It is extremely difficult to produce homogeneous aerosols by powder dispersal. Problems due to particle cohesion arise if an attempt is made to disperse powders of particle size much less than 10 µm. This is a complex problem and such factors as particle shape, material, electrical charge and moisture content are all important.

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*$10^3$ psi = 6.89 N mm$^{-2}$

†1 ft min$^{-1}$ = 5.08 × $10^{-3}$ m sec$^{-1}$

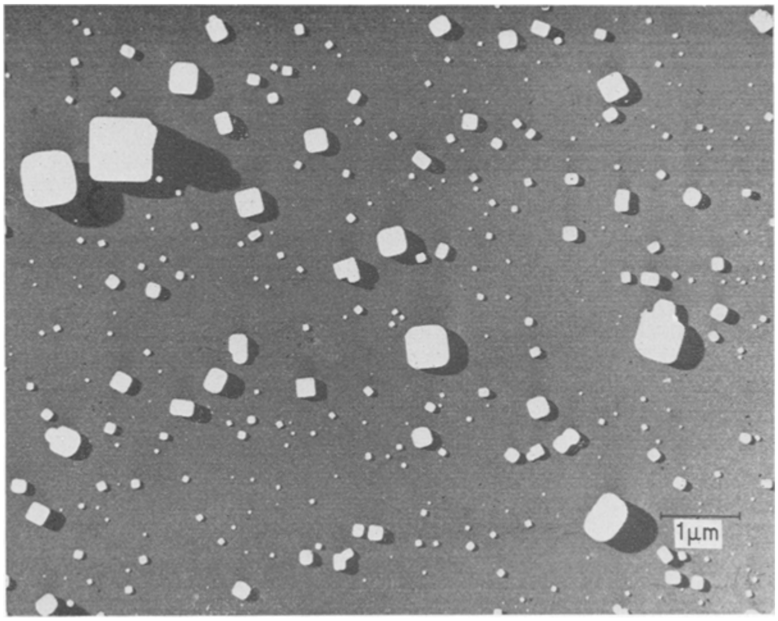

*Figure 4* Electron microphotograph of salt crystals from an aerosol. (Supplied by Chemical Defence Establishment, Porton.)

### 3.2. Centrifugal dispersion

The centrifugal atomization of liquids is especially important as it is probably the best dispersion method for producing monodisperse aerosols of controllable droplet size ranging from a few microns to over 100 µm. Rotating disc sprayers are used industrially in humidifiers, oil-fired boilers and for painting. In scientific work, disc sprayers have been widely used in agricultural and biological investigations.

Walton and Prewett [9] first drew attention to the stability of spinning-disc atomizers for producing monodisperse sprays of liquid. They fed liquid onto the top centre of a metal disc spinning about a vertical axis so that it spread as a film over the surface of the disc to the edge, where it was thrown off as a spray by centrifugal force. Low-speed measurements were performed with a disc mounted on the end of a motor-drive shaft. For high-speed testing, in which speeds of several thousand revolutions per second were attained, a Beams [10] high-speed air-driven top was used. In this design the rotating top was relatively large compared with the supporting air base. Provided care was taken to feed the liquid to the centre of the top, the mass-flow rate was low, and the liquid properly wetted the top surface, then a monodisperse spray was thrown off the edge of the disc. A much finer spray of satellite droplets was simultaneously produced. Fortunately, due to the relatively low mass of the satellite droplets they were ejected a much smaller distance from the atomizer than were the primary droplets and this enabled the satellites to be fairly easily removed. Furthermore, the mass-flow rate of the satellites was very much less than that of the primaries. Due to the monodispersity of the primary droplets they were all thrown approximately the same distance from the source. Satellite droplet removal may be accomplished by using an appropriately positioned baffling disc or more neatly by applying suction to an annular gap surrounding the disc. A suction method was used by Walton and Prewett, which complicated their atomizer and necessitated the use of a suction line in addition to the air-pressure drive line.

One problem that arose with Walton and Prewett's spinning top was that it tended to become unstable and jump from the stator at speeds of about 2000 rps. May [11] produced an improved version of the air-driven top by using a top which was relatively small, compared with the Beam's design, and it "sat" within the air-base region as shown in the schematic diagram in Fig. 5. This design proved to be relatively stable and measurements were carried out at speeds of up to 6000 rps. In addition, the drive

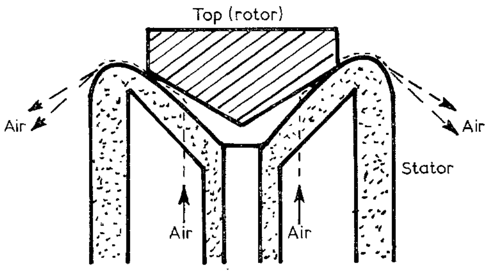

*Figure 5* Air-driven top to produce droplet sprays by centrifugal force.

air flow from the atomizer no longer rose upwards around the top and interfered with the droplets leaving the disc, but flowed over the stator surface and away downwards. May cleverly used this downward flow to entrain the satellite droplets thus removing the need for both baffles and a suction line.

Walton and Prewett's simple explanation of the drop-formation mechanism assumed that a rim of liquid accumulated on the edge of the disc until it broke away by centrifugal forces. Rapid collapse of the rim then occurred and droplets were formed according to Lord Rayleigh's [12] theory of the stability of a liquid column. Walton and Prewett assumed a proportionality between the outward centrifugal forces (drop mass × radial acceleration) and the restraining surface-tension forces (surface tension × drop diameter) giving,

$$d\omega(D\rho/T)^{1/2} = \text{constant}$$

where $d$ = drop diameter, $\rho$ = liquid density, $T$ = liquid surface tension, $D$ = disc diameter and $\omega$ = angular velocity. Experimentally, the above relationship is fairly well followed, although as far as the formation mechanism is concerned, it appears from photographic evidence [1, 13] that liquid threads rather than a rim of liquid are first thrown out from the edge of the disc.

Since the early work in 1949 on spinning-disc atomizers they have been used by Whitby *et al.* [14] for producing radioactive aerosols during lung studies, and by others doing similar work. Tracheobronchial clearance studies were carried out by Camner *et al.* [15] again using aerosols with radioactive tracers. Tarroni [16] has described a centrifugal disc atomizer with rotation speeds of up to 6500 rps. His disc was 1.6 cm in diameter and weighed 3.3 g and was used to produce aerosol particles of polystyrene down to 0.1 μm by the evaporation of droplets of a solution of polystyrene in xylene. Philipson [13] used an electronically controlled spinning disc at speeds of just over 1000 rps to produce aerosol particles of polystyrene from a solution. Particle size was within a standard deviation of 4%. Some excellent photographs of droplets breaking away from the spinning disc were obtained by using a 15 nsec illuminating pulse from a Q-switched ruby laser.

### 3.3. Electrostatic dispersion

An electric field normal to the surface of a conducting liquid induces surface charges, which set up "outward" electrostatic forces which oppose the binding surface-tension forces of the liquid. A sufficiently high field can disrupt a liquid surface so that an aerosol spray of charged droplets is produced. The first recorded investigations of this phenomenon were by Bose in 1745 [17] who worked with a liquid which was brought to the end of a glass capillary tube, where it was disrupted into an aerosol spray, due to a high potential applied to the capillary. Zeleny [18] investigated electrostatic spraying from a capillary and showed how the potential required for liquid-surface disruption was related to the surface tension. Although electrostatic dispersion usually produces a polydisperse aerosol, Vonnegut and Neubauer [19] found that in certain poorly-defined circumstances, they were able to produce a fine smoke, which when illuminated by a parallel beam of light, showed Higher-Order Tyndall spectra (see Section 5.2.1) which indicated a high degree of monodispersity with a droplet size of about 1 μm.

Electrostatic dispersion of a liquid may take place in a gaseous environment such as the atmosphere, or in vacuum. The environment may well impose limiting conditions upon the aerosol formation process, due to corona discharge. This is readily appreciated by considering what probably occurs during the dispersal process. Spraying from a liquid surface emanates from well-defined sites. These sites arise when localized surface charge is high enough to cause transitions from the initial surface position to conical protrusions or spikes, the apices of which are stretched out into ligaments of liquid which collapse into droplets due to Rayleigh instabilities. Taylor [20] showed theoretically and experimentally that liquid cones were stable for apex angles of 98.6%. During electrostatic dispersal of a liquid many spraying sites coexist and considerable localized variations in field, and other factors, will result in variations in the geometry of the different sites. However, as filaments of liquid are formed, with very small radii of curvature, the local electric field will rise as it is inversely proportional to filament radius. A corona discharge will often ensue under atmospheric conditions and this will have the effect of limiting droplet size to the same order as that of the filament diameter at the corona limit. In practice, in electrostatic paint sprayers for instance, drops are not produced much below about 1 μm in diameter and paint sprayers usually operate under corona-discharge conditions, the corona being just discernible in the dark. There is usually no such limitation on droplet size when liquids are dispersed *in vacuo* although with high-vapour-pressure liquids it is possible for discharge to arise due to vapour breakdown. Strictly speaking, dispersion into a vacuum does not produce an aerosol, as we are dealing with a single-phase system which will settle. Often the definition of the word aerosol is used rather loosely under these circumstances.

It is important to realize that electrostatic dispersion produces a charged aerosol. Aerosols generated from a source at a positive potential are positively charged and negatively charged from a negative source. Charge tends to confer some degree of stability on the aerosol in that coalescence of particles is less likely. If the solid particles in a fluidized bed are charged by, say, a corona discharge, there may be a considerable rise in the height of the cloud, due to electrostatic repulsion between particles.

## 4. Aerosol formation by condensation

Aerosol droplets may be formed by condensation from a supersaturated gas either spontaneously, if the supersaturation is high, or by stimulation using nucleation centres. Spontaneous condensation has been studied by many workers and theory has been fairly well substantiated experimentally. Lord Kelvin [21] established a relationship for a droplet in equilibrium with its vapour which is usually referred to as the Gibbs-Thomson equation and it is given by:

$$\ln(P/P_\infty) = 2\gamma M/RTpr$$

where $r$ = droplet radius, $M$ = liquid molecular weight, $\rho$ = liquid density, $\gamma$ = liquid surface tension, $R$ = gas constant, $T$ = absolute temperature, $P$ = vapour pressure surrounding droplet and $P_\infty$ = equilibrium vapour pressure at a plane liquid surface. A hyperbolic relationship thus exists between ln $(P/P_\infty)$ and droplet radius which defines a critical-drop size below which the drop will evaporate and above which it will grow. For any given supersaturation, $P/P_\infty$, condensation should ideally occur uniformly throughout the volume of the supersaturated gas phase as embryonic droplets of the critical size, given by the Gibbs-Thomson equation, are spontaneously formed. The higher the initial degree of supersaturation the more rapid is the condensation, which leads to a rapid reduction in the supersaturation, thus inhibiting further spontaneous condensation. All droplets are therefore formed during a very short interval of time so that a monodisperse aerosol is produced. Furthermore, the rate of increase in radius of droplets is inversely proportional to radius so that even if droplets are, at some early stage, of slightly different sizes these differences rapidly become insignificant and the system becomes more monodisperse.

In practice it is not easy to produce a uniform supersaturated gas. If supersaturation is produced by adiabatic expansion of a saturated gas, for example, precipitation is likely to occur before the expansion is complete, that is before the maximum supersaturation is attained so that nucleation does not occur simultaneously throughout the phase. Methods which rely upon cooling a saturated gas by mixing with cooler gas are likely to produce polydisperse aerosols due to condensation occurring before a homogeneous mixture is established. For the above practical reasons polydisperse aerosols tend to form by condensation unless extreme care is taken. Virtually all authors report that polydisperse aerosols are formed in the absence of nucleation centres. Fletcher [22] has considered the theoretical and experimental aspects of spontaneous condensation. Barkow [23] by repeated adiabatic expansion of moist air was able to remove undesirable nucleation centres and eventually produce very monodisperse mists.

Condensation induced by seeding a supersaturated gas is a well-established method of producing monodisperse aerosols. For condensation to occur one would expect seed particles of size at least equal to that of the critical drop size to be required. This conclusion is not validated by experience and many workers have discussed the problem at great length. Clearly the physical characteristics of a seed particle such as its shape, surface state, chemical composition, etc, will influence its seeding ability. If a monodisperse aerosol is to be produced by seeding, the seed particles must have as near identical characteristics as possible. After condensation has occurred it is necessary to minimize the chance of particle coagulation and dilution of the aerosol by mixing with pure gas is often necessary. Fuchs and Sutugin [24] state that if coagulation is to be unimportant then the droplet concentration should not exceed $1.7 \times 10^8$ cm$^{-3}$ for an experimental time of 1 sec and $2.8 \times 10^5$ cm$^{-3}$ for a time of 10 min.

### 4.1. Sinclair – La Mer apparatus

Fig. 6 shows schematically the monodisperse aerosol generator first used by Sinclair and La Mer [25]. Some improvements to this type of generator have since been made by Muir [26]. The hot liquid to be dispersed is contained in flask A and a fog is produced by bubbling air through it from the immersed end of a tube. Air is also passed through the "seed formation flask" B in which nucleation centres are formed, possibly by means of spark discharge as in the original apparatus. A fog containing nucleation centres flows from flask A via nozzles to flask C, which is at a higher temperature than A, and liquid droplets in the fog evaporate so that a saturated gas containing nucleation centres is formed. This mixture flows up a chimney and cools and at the same time uniform condensation occurs. Further mixing with air may take place at the outlet to minimize coagulation. The size of the aerosol particles depends upon the initial vapour concentration and a measure of control of size may be obtained by varying the temperature of the liquid in flask A, and by altering the air bubbling rate through the liquid. The Sinclair-La Mer generator may be used to produce particles in the size range from well below 1 µm to about 30 µm.

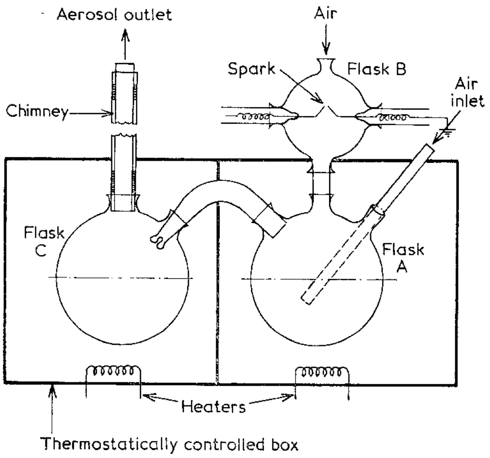

*Figure 6* Sinclair-La Mer condensation apparatus.

### 4.2. Rapaport – Weinstock apparatus

Fig. 7 shows an apparatus which was developed by Rapaport and Weinstock [27]. It is simpler and cheaper than the Sinclair-La Mer apparatus and is of comparable performance. It has a start up time of only about 10 min compared with a time of several hours for the other generator. A liquid containing non-volatile impurities is atomized using a blast of filtered air to produce a polydisperse aerosol which is blown towards the wall of the reservoir. This has a baffling effect and many larger droplets are removed. In flowing upwards through the chimney, further large droplets are lost until only droplets below 1 µm

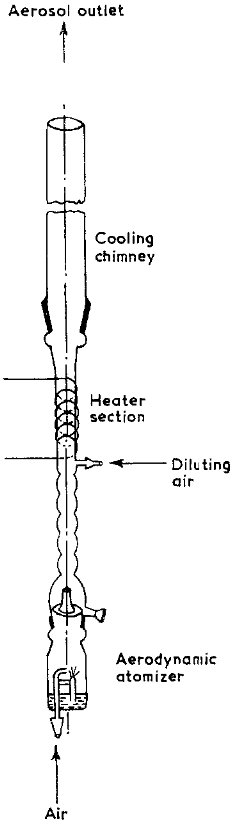

*Figure 7* Rapaport-Weinstock condensation apparatus.

remain. Filtered air may be injected into the chimney for dilution purposes. Droplet evaporation is induced in the heater section above the chimney so that a vapour-gas mixture plus non-volatile impurities from the droplets is produced. Condensation then occurs in the cooling chimney above the heater section as in the Sinclair-La Mer apparatus. Preparation of the liquid for use in the Rapaport-Weinstock apparatus is clearly, critically important.

Finally, it should be mentioned that Liu *et al.* [28] have worked with a generator similar to the one described above. In addition Tomaides *et al.* [29] describe an even more sophisticated version in which a small percentage of aerosol is extracted from the centre of the stream from the condensing tube. They claim that a more monodisperse aerosol can be produced in this way.

## 5. Measurements of aerosol characteristics

In considering aerosol diagnostics we are primarily concerned with determination of particle-size distributions and densities. If we are attempting to diagnose an "unknown" aerosol we may in addition seek information on particle shape, material, refractive index and whether or not particles are electrically charged. These latter aspects of particle characteristics will not be considered here. Diagnostic methods may be classified as direct when particle size distribution and densities are measured directly by observation of individual particles either, *in situ*, or by sampling and collection. Indirect diagnosis is concerned with inference of aerosol microstructure by observation of macroscopic behaviour. Most indirect diagnosis is based upon the interaction of visible radiation with the aerosol, and Mie scattering theory is usually applicable.

### 5.1. Direct diagnostic techniques

#### *5.1.1. Micro-photography*

Direct photography of aerosol particles is possible but is of limited usefulness due to restrictions imposed by lenses on the field of view and the depth of focus.

The minimum particle diameter, $d$, that can be resolved optically is given by classical theory as

$$d = 0.61\ \lambda/A$$

where $\lambda$ = wavelength of the illumination and $A$ = numerical aperture. By considering an objective with the highest available resolution, particles of less than about 0.2 μm cannot be theoretically resolved by visible light. In practice it is possible to do slightly better than this as with separated particles it is sufficient to discern only the first diffraction ring due to a particle, to detect it. Walton *et al.* [30] detected particles of methylene blue of 0.13 μm diameter in this way.

Photography seems to be especially useful for monitoring droplet formation processes, as is exemplified by the many excellent photographs which appear in papers by Dombrowski *et al.* [2, 3] and also by Fig. 2. No other technique can yield so much information about liquid film and filament disruption as a direct photograph, or better still a film of the phenomenon.

#### *5.1.2. Holographic techniques*

The development of in-line holography for the measurement of small particles follows from the work of Silverman *et al.* [31]. Their initial paper entitled "A laser Fog Disdrometer" described how holograms of fog particles could be recorded using a Q-switched ruby laser. A hologram is essentially a photographic record of the diffraction patterns which are produced when particles are illuminated by a coherent, collimated, quasi-monochromatic beam of light. In their paper, Silverman *et al.* determine the particle sizes and positions by interpreting the diffraction patterns (i.e. the hologram) but difficulties with this technique could arise if non-spherical particles were to be studied, or if two particles were so close that their diffraction patterns overlapped. These difficulties were overcome by using a continuously operating He–Ne laser to reconstruct the original three dimensional particle field from the two dimensional hologram, as described by Thompson *et al.* [32]. A diagram of a holographic recording system and a reconstruction system is shown in Fig. 8. The pin hole acts as a spatial filter, in that it enables a suitably coherent portion of the laser output to be selected. Pin hole diameters of about 100 μm are suitable. A microscope may be used to view the reconstructed image of the aerosol, in place of the TV camera, but in practice the latter is often found to be more convenient. The system described by Thompson *et al.* operated over a particle diameter range of 4 to 200 μm.

When the aerosol sample is illuminated by the pulse of radiation from the ruby laser diffraction patterns are recorded photographically, in a plane, in the far field of the individual particles but in the near field of the whole sample volume.

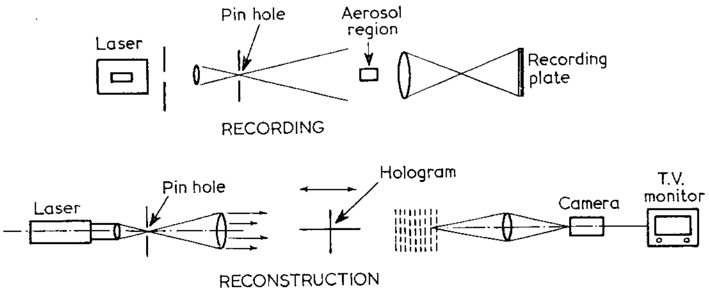

*Figure 8* Recording and reconstruction of holograms.

Distinctive Fraunhofer diffraction patterns are recorded corresponding to each particle. These patterns contain enough information to completely locate each particle during the brief time of the laser pulse. The particles are, in fact, effectively "frozen" in position. The illumination of the hologram by a CW laser enables the original sample volume to be reconstructed and it may be inspected in detail with a microscope to determine particle size, shape and position. Fig. 9 shows a hologram of 85 μm diameter maize-pollen particles which have been dusted onto 5 μm diameter perspex fibres. Fig. 10 shows the reconstructed images formed from the hologram of Fig. 9. The straight criss-crossing lines are the perspex fibres. The above two photographs were taken by R. Bexon of the Chemical Defence Establishment, Porton.

Lenses are not essential in holographic recording and reconstruction, but may be used to enable the full resolution capability of the film to be realized. The use of lenses enables the optimum aerosol sample size to be recorded on a single film. The effective depth of focus of the holographic system is several orders of magnitude greater than that of a microscope system. If a plane wave is used for recording and reconstruction the magnification of reconstructed particles is uniform over the entire recorded volume. If a ruby laser operating at a wavelength $\lambda_0$ of 694 nm is used for recording and a He–Ne laser operating at a wavelength $\lambda$ of 633 nm is used for reconstruction, a slight demagnification of $\lambda/\lambda_0$ will occur but may be compensated for by magnification, by the use of lenses and also by the "geometry of the system" as discussed by Thompson *et al.* [33].

Many of the normal photographic techniques which are useful in the study of dynamic systems may be used in holography. Holographic motion pictures may be made and stroboscopic techniques may be applied. A Q-switched laser is used for illuminating purposes. Fourney *et al.* [34] describe a system based upon a Q-spoiled ruby laser which emitted two equal energy giant pulses with a known time interval between them. The system was tested by measuring water droplets in a spray and it was possible to determine a histogram size distribution curve with 2.5 μm intervals for droplets greater than 5 μm in diameter.

Pavitt *et al.* [35] demonstrated the feasibility of measuring the size distribution of water droplets (size range 10 to 100 μm) moving at velocities of up to 100 m $\sec^{-1}$ using in-line holographic techniques. The intention was to determine whether it would be possible to measure cloud droplet distributions from an aircraft. A pulsed ruby laser was used for recording the hologram and a CW He–Ne laser was used for reconstruction. The system differed slightly from earlier systems in that no lens was used to form a real image of the aerosol for recording purposes. The only lens used in the recording system was to produce a divergent beam from the laser. The "lensless" system was used as it has a larger effective aperture and hence a larger aerosol volume may be sampled than with a lens system of the sort used by Thompson *et al.* To simulate cloud conditions two ultrasonic atomizers were used at frequencies of 20 and 100 kHz. They generated water droplets in the ranges 30 to 60 μm and 15 to 25 μm respectively. Each atomizer could be separately mounted in a wind tunnel in which a rotameter was used. It was shown that droplets in the above ranges were satisfactorily recorded at distances of up to 13 cm from the recording system but experimental limitations prevented the full potential of the technique from being

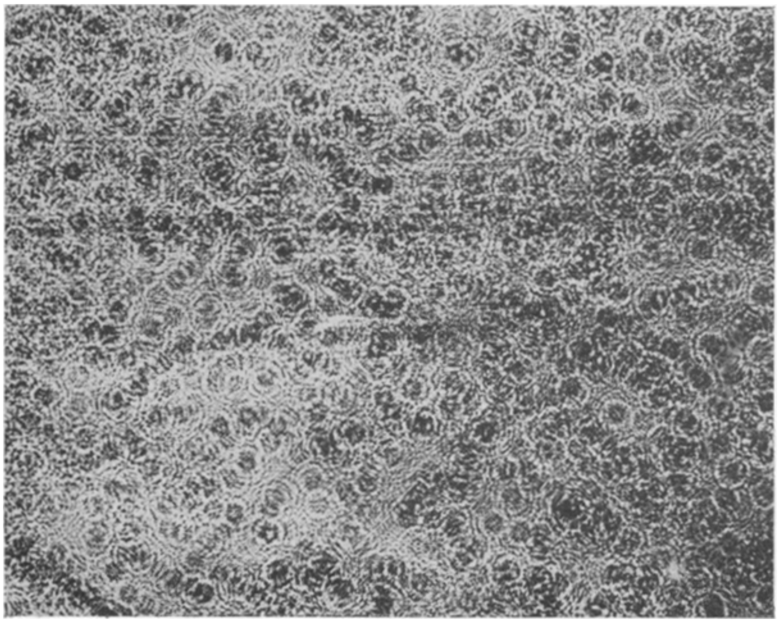

*Figure 9* Hologram of 85 µm diameter maize pollen particles on 5 µm diameter perspex fibres. (Supplied by CDE, Porton.)

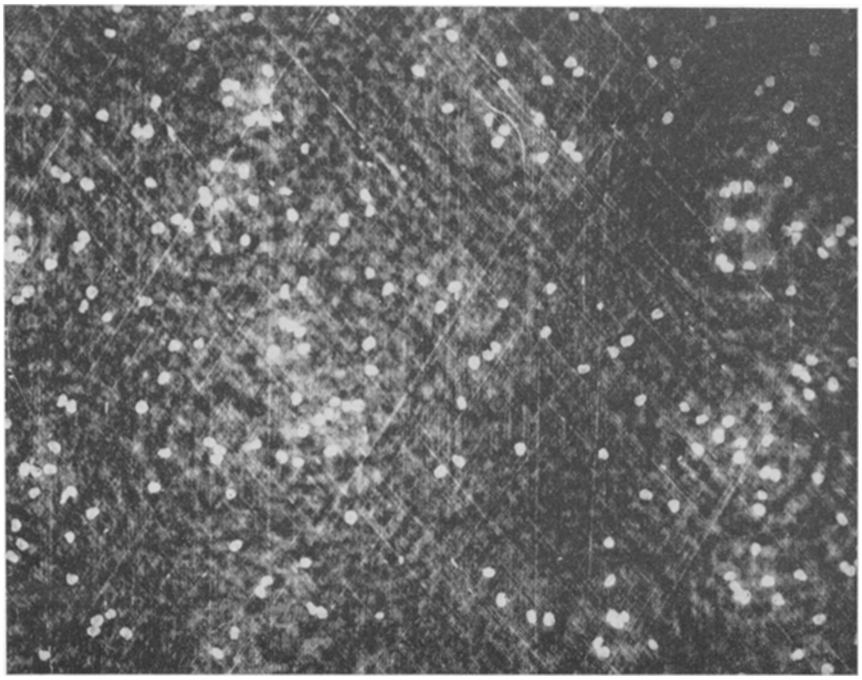

*Figure 10* Reconstruction of particle field from above hologram. (Supplied by CDE, Porton.)

realized. It was possible to sample aerosol volumes of about 0.5 litre.

Pavitt *et al.* [35] considered the theoretical limits of their system with respect to the following five factors:

(1) coherence of the reconstruction beam;
(2) resolution of the recording emulsion;
(3) noise introduced by the emulsion;

(4) coherence of the recording beam;

(5) motion of the droplets.

It was concluded that factors 1 and 2 imposed no limitation on the resolution of the system. Factor 3 was not important either, for the cloud sampling application being considered. However, noise due to the emulsion produces a characteristic mottling effect on the recording which could be serious if the droplet image brightness fell below a certain level. The fourth factor, coherence of the recording beam, was considered to be the most important limiting factor to the resolution of the system. With a spatial coherence of about 2 cm a resolution limit of about 7 μm was estimated for a particle 10 cm away from the recording system. In considering the fifth factor, it is a simple matter to show that with a recording pulse of typically 20 nsec duration a droplet would travel only 2 μm at 100 m $\sec^{-1}$ and so blurring only becomes important for particle sizes below about 10 μm.

Bexon [36] considers the magnification of the in-line holographic system. He expresses the overall magnification of the system, $M$, as

$$M = m_0 m_i m_a$$

where $m_0$ is the magnification brought about by the recording configuration. For a fixed source/hologram distance, magnification increases as the object is brought closer to the source. $m_i$ is the magnification introduced in the reconstruction process and may have one of two values depending on the distance of the hologram from the reconstruction source. $m_a$ is the auxiliary magnification of the optical viewing system. Magnification of an object can be determined accurately without any knowledge of the distance of the object from the hologram during recording. During reconstruction, using a fixed distance, $d$, between the source and the image plane (viewing position) each plane of the aerosol object may be brought into focus by moving the hologram, provided $d$ is greater than 4 × focal length of the plane to be reconstructed. It is explained how this condition may readily be fulfilled. The system was tested using maize pollen grains of diameter 85 μm but particles of size down to 4 μm have also been reconstructed. Magnifications of over 200 were used without undue image deterioration.

### *5.1.3. Particle collection*

Particle collection, in the widest sense, is the extraction of a large proportion of particles from an aerosol by filtration, sedimentation, precipitation, etc. As far as aerosol diagnosis is concerned a small representative sample only of particles is collected, and a few methods which are commonly employed will be outlined. It is essential that the sampling method be equally efficient for all particles in the size range. Sampling must not perturb the size distribution. This apparently straightforward requirement is far more difficult to satisfy than might be expected. A brief mention of some of the special problems that can arise will illustrate this point. If particles are to be sampled from a still aerosol the natural settling of particles due to gravity may be important. Stokes' law states that the settling velocity of a spherical droplet is proportional to the square of its diameter so that the largest droplets of an aerosol will settle out first. If solid particles are present the settling rate may not be simply related to the volume of a particle as such factors as shape and density must be accounted for. Whatever the particle composition, solid or liquid, Stokes' law of settling indicates that gravity will select certain particles and this selection will be time dependent. Brief sampling times will result in samples which contain a greater proportion of heavier particles than exist in the aerosol. As sampling time is increased a greater number of lighter particles settles out.

When considering applications which depend upon settling of particles, in dealing with insecticide sprays for example, it is convenient to evaluate the "dosage" of the aerosol. Dosage is a measure of the deposition ability of a substance and is given by the product of the concentration of the aerosol (mass or volume of particles per unit volume) and the exposure time of the collecting area. As aerosol concentration may be time dependent it is often necessary to integrate over the duration of the exposure to evaluate dosage.

In considering deposition of particles from the atmosphere very many factors may influence the results. Factors which effect particle concentration at the collecting point are normally considered and these range from the proximity and altitude of the source or sources to consideration of the type of terrain between source and measurement point together with careful consideration of all atmospheric conditions which might be important (turbulence, winds, temperature gradients, etc).

There are several most interesting effects which may arise in the vicinity of a collecting surface and these may be responsible for collected samples of particles with size distributions which are non representative of the aerosol. Three such effects are named photophoresis, thermophoresis and diffusiophoresis. Photophoresis refers to particle movement induced by light. It arises due to absorption of radiation which results in a non uniform temperature rise of the surface; particle interaction with the surrounding gas then sets up forces which move the particle. All types of particle trajectory arise, generally with a nett drift in a direction dependent upon the direction of the light source. Photophoresis may act in conjunction with other forces arising from magnetic, electric or gravitational fields.

Tyndall [37] observed a dust-free zone surrounding a hot body in a dusty environment. This apparant repulsion of particles from a hot body is known as thermophoresis and results from a temperature gradient in the gas. A nett force is exerted on the particles driving them away from the higher temperature regions. The force arises from an imbalance in the momentum transfer to the particles due to collisions with gas molecules.

Concentration gradients in a gas may induce a drift of particles which is usually in the same direction as the drift of the heaviest component of the gas. This so called diffusiophoresis was observed by Facy [38] when he detected a dust-free zone surrounding an evaporating water drop. Conversely, a salt particle taking up moisture from the surrounding gas attracts dust particles to itself.

A few physical effects which may possibly be of importance during aerosol sampling have been briefly mentioned. Other effects due to Brownian motion, electric charges, radioactivity, etc, may be important in special cases. Almost invariably the collection of a representative sample of particles from an aerosol is a task fraught with difficulties of one sort or another. There is sometimes a danger that the collection process will actively upset the size distribution of a collected sample by allowing coagulations or disintegrations which would not otherwise have occurred. The collection of droplets may pose special problems due to evaporation from the collecting surface. In addition the collected droplets of liquid will often be non spherical. Once particles have been collected it is necessary to observe them by a high power optical microscope or an electron microscope so that counting and sizing may be carried out. This may be done visually or automatically. Counting and sizing methods will not be discussed.

A common particle-sampling technique used for optical microscopy is to position a specially prepared microscope slide in the aerosol for a short time so that particles settle or impact onto the surface. There are three long-established and well known slide-surface-preparation methods which have been fully described by May [39, 40]. The first method which uses a "bare" clean glass slide for droplet collection is known as the focal-length method. Collected droplets distort to form plano-convex lenses with a well-defined liquid-glass contact angle which depends upon surface condition and the liquid collected, but is essentially constant for droplets of different sizes of the same liquid. Microscopically the focal length of each collected droplet is measured using a calibrated fine adjustment on the microscope; the droplet lens diameter is also measured. Knowing theoretically the droplet lens geometry and the refractive index of the liquid the undistorted droplet diameter may be calculated. This method is lengthy and tedious and cannot be used with highly volatile liquids. In practice it is difficult to determine the focal point of lenses smaller than about 5 μm.

A second method of droplet sampling which is sometimes called an "absolute" method uses a slide whose surface is covered with a layer of gelatinous substance of density similar to that of the droplets but of different refractive index. Gelatine/water/glycerol mixtures are useful when intercepting oily droplets. After sampling the aerosol, a warmed cover slide upon which is a large blob of the gelatinous substance is placed on top of the sampling layer to form a "sandwich". Due to the warmth, the droplets resume spherical shapes in the melted medium, which soon resets. Droplet sizes may then be determined directly using a microscope. This method is cumbersome and coalescence of droplets can occur if too dense a particle sample is intercepted. Once a slide has been prepared, it may be stored for quite a long time.

The third sampling method has been in use since 1941. A glass slide surface is coated with magnesium oxide simply by burning magnesium ribbon underneath the slide. A layer at least as thick as the droplet diameter is required. The grain size of the magnesium oxide is about 0.5 μm. Droplets striking the surface layer leave well-defined, circular holes which are viewed microscopically with transmitted light. Bright spots are seen against a dark background. May calibrated this method of droplet size determination against the previous two methods by using a Walton and Prewett spinning disc droplet source. He also determined the importance of impact velocity upon the accuracy of the method. He concluded that a factor of 0.86 should be applied to the measured sizes of holes made by droplets larger than about 20 μm of *any liquid* at *any impact velocity*. This factor should be reduced for droplets of sizes less than 20 μm and the method is only applicable for droplets down to about 10 μm in diameter. The method is simple and quick to apply and no coalescence of droplets can occur after collection. The layer is, though, rather fragile.

Several investigators have described droplet sampling methods in which freezing of a collected sample is used. Taylor and Harmon [41] froze water droplets in hexane cooled to about −20° C with solid carbon dioxide. Choudhury *et al.* [42] used liquid nitrogen to freeze a whole range of substances.

Street and Danaford [43] describe a method whereby a Petri dish filled with liquid nitrogen is momentarily inserted into a diesel oil spray. Droplets are frozen and sink to the bottom of the dish without agglomerating. The nitrogen is then allowed to boil off and the droplets are photographed directly under a microscope using transmitted light. After boil-off a few minutes elapses before diesel oil droplets melt. The amount of contraction that occurred due to freezing was about 2 to 5% depending upon the substance that was frozen.

The foregoing discussion has been confined to sampling techniques which are suitable in conjunction with optical microscopy. However, for particle sizes below about 0.5 μm the electron microscope must be utilized and this instrument has a claimed resolution of about 0.001 μm. Electron microscopy is principally used for studying solid particles although it may be used rather indirectly for studying liquid droplets. Harris [44] for instance electrostatically precipitated relatively non-volatile droplets onto wet gelatine where they spread to form lenses. After the film had dried the droplets were dissolved away in solvent leaving concave depressions in the gelatine surface. A carbon replica of this was made which could be photographed using the electron microscope. Calculations were then required to determine the original size of the droplets. Harris [45] subsequently improved upon this technique.

To study solid particles with the electron microscope aerosol particles must be collected on a surface. Often a collodion film is used so that shadow casting, as described by Williams and Wyckoff [46], may be used to enhance the appearance of the particles. Alternatively, a replica of the collected sample is made. Green and Lane [1] describe several techniques of sample preparation.

### 5.2. Indirect diagnostic techniques

Lord Rayleigh [47] considered theoretically the scattering of light by particles much smaller than the wavelength of light and was able to explain such natural phenomena as the blue of the sky and the red of a sunset. Rayleigh's theory is applicable to scattering of visible light by particles up to a size of about 0.03 μm and is thus of limited use in aerosol studies. A more general theory of scattering based on electromagnetic theory was developed by Mie [48] in 1908. More recent developments of the theory have been covered by Van de Hulst [49] Kerker [50] and others. Mie's theory is valid for particles of sizes within the Rayleigh range of applicability and above and is used as the basis of several indirect methods of measuring particle size in aerosols. However, it needs to be emphasized that the theory is strictly applicable only to monodisperse aerosols consisting of spherical, homogeneous particles of known optical properties. Mie theory was, until the early 1940s of limited use due to the enormous amount of calculation required in order to interpret optical measurements. Tables of functions became available in 1941 which enabled the required calculation to be reduced substantially. In 1949 Lowan *et al.* [51] directed the preparation of tables of scattering functions for spherical particles at the National Bureau of Standards. Since then, with the widespread use of computers, the application of Mie theory has become even easier and there are programs available for calculating the scattering function [52]. In addition to these benefits of the computer, much experience has been gained of the optical properties of more complex aerosols consisting of irregularly shaped particles. It is inappropriate to attempt to detail Mie theory in a review of this sort and in any case this has been admirably done by others [49, 50]. Instead, just sufficient information will be presented to enable the salient features of the experimental techniques, based on Mie theory, to be appreciated.

A beam of light incident upon an aerosol cloud will be partially scattered and absorbed by the aerosol particles and an attenuated beam will be transmitted through the aerosol. There are three characteristics of the scattered light, from a monodisperse aerosol, which may be measured and used in diagnosis, i.e. 1. colour, 2. polarization, 3. intensity.

In addition, it is sometimes possible to measure the attenuation of transmitted light through the aerosol. This method requires that the aerosol is not too sparse, or if so, a long path length of light transmission is required. The equipment required for attenuation measurements is relatively simple, and, if applicable, attenuation measurements are to be preferred to the much more complex, scattering measurements.

When a plane wave of light of unit intensity is incident upon a spherical particle the total intensity of the scattered light, $S$, is given by:

$$S = \frac{\lambda^2}{2\pi} \sum_{n=1}^{\infty} (2n + 1)(|a_n|^2 + |b_n|^2)$$

where $\lambda$ = wavelength of light and the functions $a_n$ and $b_n$ are complex functions of the parameter $\alpha$, where $\alpha$ = particle circumference/$\lambda$ and the particle refractive index, $m$. For transparent, non-absorbing spheres, $m$ is real but for absorbing spheres $m$ is complex. The intensity, $I_\theta$, of scattered light is a function of the angle $\theta$ between the direction of propagation and scattered light, and is given by

$$I_\theta = \frac{\lambda^2}{8\pi^2 R^2}(i_1 + i_2)$$

where the functions $i_1$ and $i_2$ are proportional to the intensities of the two incoherent, plane-polarized components of the scattered light. $R$ is the distance from the particle to the point of observation.

### *5.2.1. Measurements of the colour of scattered light (higher order Tyndall spectra)*

The particle size of a monodisperse liquid-droplet aerosol may be determined fairly readily by observing the colour of scattered light as a function of the viewing angle A portable instrument which was specially built for this purpose was described by Sinclair [53] and was code named "Owl". The aerosol is admitted to a cylindrical chamber with transparent sides and is illuminated from the side with an unpolarized white-light beam. Scattered light at various angles, $\theta$, to the incident beam is viewed through a low-power microscope. Observations at angles in the range 15° to 165° may be made and read from a scale. A sequence of bright colours is seen as $\theta$ is varied and the colours may be enhanced if observation is made through a plane polarizer which cuts off the $i_2$ polarization, which usually exhibits less distinct colours than the $i_1$ wave. The observed sequence of colours repeats itself with a periodicity which increases with droplet size. The purity and brightness of colours increases with the degree of monodispersity. Measurements of droplet size are made by counting the number of times that the colour red is observed over a measured angular range. This method of size determination is useful for particles with radii in the range 0.1 to 1 μm.

### *5.2.2. Measurements of the polarization of scattered light*

With slight modification the "Owl" may be used for polarization measurements. The eyepiece is fitted with a split-field polarizer disc, one half with its polarization direction parallel to the dividing line and the other half normal to it. In addition a filter is used, usually between the polarizer and the eye, so that polarization at a known wavelength is measured. For values of $\alpha$ below about 2.5, and for viewing angles of about 90° the ratio of the two polarizations $i_2/i_1$ is a single-valued function of $\alpha$ and may be used to measure particle size. Sinclair and La Mer [25] used this method at $\lambda = 0.524$ for radii from 0.05 to 0.2 μm. At a fixed viewing angle of about 90° the polarizer disc is rotated until the two polarization intensities appear to be equal. If the angle between the dividing line of the disc and the plane of observation is $\phi$, then:

$$i_2/i_1 = \tan^2\phi\,.$$

Values of $i_2$ and $i_1$ for different particle sizes and different refractive indices are available in tables, and it is a straightforward matter to determine particle size. The polarization method of determining particle size is restricted to values of $\alpha$ below 2.5 which means it is only applicable for droplets of radii of about 0.2 μm and below.

### 5.2.3. Measurements of the intensity of scattered light

Droplet size of a monodisperse aerosol may be determined by measuring the intensity of scattered light over a considerable range of scattering angle and then by integrating the intensities over a sphere. The method is tedious and not particularly accurate and is little used. However, if particle size is known, then an intensity measurement at any scattering angle provides a sensitive method of determining particle concentration.

One interesting application of this method of measurement is for diagnosing the size distribution of a polydisperse aerosol. At a fixed wavelength, the Mie equation may be approximated over a small range of values of particle radius, by the expression

$$I = knr^p$$

where $k$ and $p$ are constants, $n$ = number concentration of particles and $r$ = particle radius. This expression was given in 1932 by Whytlaw-Gray and Patterson [54] but they were unable to determine the value of $p$. This was done later by Sinclair and La Mer [25] who determined $p$ as a function of $r$ for several scattering angles. For small particles, below about 0.1 μm, Lord Rayleigh's theory is applicable and $p = 6$.

To obtain information of the size distribution of a polydisperse aerosol a small volume of aerosol in the upper region of a sample is measured periodically. Assuming that initially the aerosol is uniformly distributed in the sampling chamber, Stokes' law of settling under gravity may be used to calculate the rate at which particles leave the small volume being sampled. For successive small time intervals the change in scattered light intensity $\Delta I$ is measured and the average particle size which has "cleared" the sampling region in each time interval is calculated from Stokes' law. The appropriate values of $p$ are determined from graphical data, and the decrease in particle concentration $\Delta n$ over a period may then be determined from the equation

$$\Delta n = \Delta I / kr^p .$$

### 5.2.4. Measurement of the attenuation of transmitted light

The extinction of light by aerosols can be readily measured using simple apparatus and the surface-area concentration and mean size of the particles can usually be deduced without prior knowledge of the composition and size distribution of the particles. Measurements may be made directly on the aerosol, or alternatively, particles may be deposited upon glass slides and the glass slide may then be diagnosed in place of the aerosol. A refinement of this technique is to convert the collected sample to a metal replica so that the light transmitted through the resultant field of holes may be measured. Hodkinson [55] discusses these methods.

If a beam of light of intensity $I_0$ is incident on an aerosol the transmitted beam is attenuated and its intensity $I$ is given by the Bouguer law, or, as it is often called, the Lambert-Beer law,

$$I = I_0 \exp(-\tau D)$$

where $\tau$ is the turbidity of the aerosol and $D$ is the distance travelled through the aerosol, by the radiation. The turbidity of the aerosol is defined by the relation

$$\tau = naE$$

where $n$ = particle concentration, $a$ = cross-sectional area of the particle that is projected against the beam, and $E$ = particle extinction coefficient defined as the ratio of total light flux scattered and absorbed to flux geometrically incident on the particle.

For randomly orientated droplets, their projected area concentration $na$, is approximately 0.25 of their surface area concentration, by Cauchy's Theorem. For a polydisperse system $naE$ must be found by integration over the particle-size distribution.

Proctor [56] describes a laser technique based on the attenuation of transmitted radiation, which was used for measurements on a coal-dust cloud. This work is relevant to research into pneumoconiosis and particle sizes of below 5 μm are of interest. A dust chamber was built into the cavity of a helium-neon laser operating at a wavelength of 1.15 μm. Laser output was monitored by a silicon photocell. A filter interposed between the laser and the photocell served to cut off incoherent radiation from the glowing He–Ne plasma. Experimental procedure consisted in first measuring the photocell detector current, $I_1$, with no dust in the cell, followed by a measurement with dusty air admitted to the cell ($I_2$). A final check with the dusty air removed was then done. Proctor states that the Lambert-Beer law is applicable for values of $I/I_0$ in the range 1.00 to 0.37 and all his measurements were within this range. By expanding the exponential

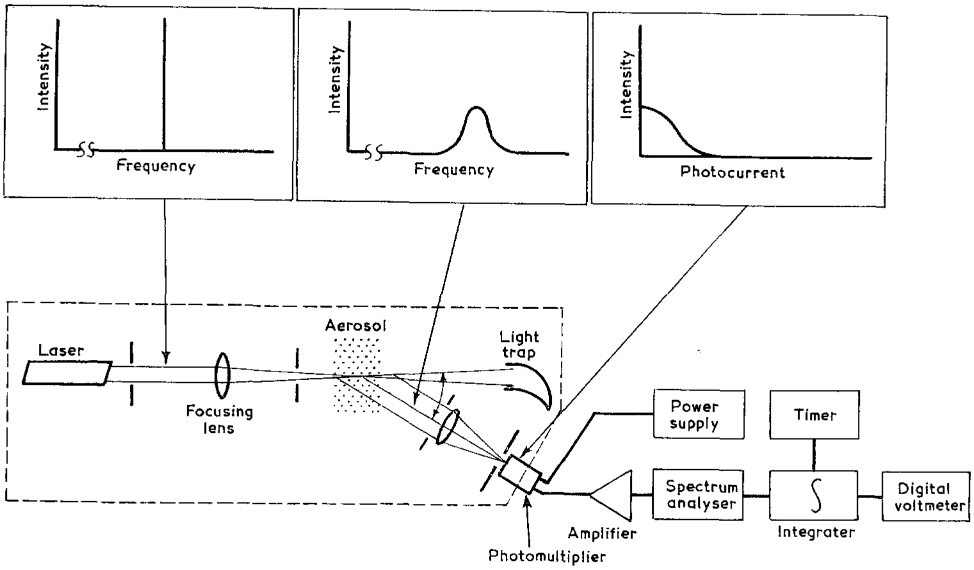

*Figure 11* Laser Doppler spectrascope for aerosol measurement.

term of the Lambert-Beer equation and assuming that $\tau D \ll 1$ so that second degree terms and higher may be neglected it follows that

$$\frac{\Delta I_0}{I_0} = \tau D\,.$$

Hence the aerosol turbidity is given by the fractional change in the intensity of illumination. In a He–Ne laser operating under normal conditions the intensity of radiation along the cavity is constant to within 3 %. In the theory of this laser method of dust measurement the fractional gain in intensity of radiation due to lasing is equated to the fractional loss of intensity due to all factors, including scattering and absorption by the aerosol particles. Proctor shows that if the laser is operating in a mode such that the unsaturated gain is much greater than the total losses, then

$$(I_1/I_2)^{1/2} = 1 + 2\tau D/A$$

where $A$ is related to the gain of the laser, and has to be determined. Proctor determined $A$ by measuring the turbidity of a dust sample independently of the laser and found $A = 0.033$ which meant that 3.3 % of the radiation within the cavity was lost by transmission through the end mirrors and by scattering and absorption when no dust was present. Proctor concluded that the He–Ne laser provides a convenient and accurate means of measuring the surface area concentration of airborne respirable dust.

### *5.2.5. Laser Doppler spectroscopy*

The Brownian motion of aerosol particles causes Doppler frequency shifts in the scattered light from each particle. An analysis of the frequency information present in the scattered light from a particle ensemble undergoing Brownian motion has been given by Pecora [57] who predicted that the scattered light would have a Lorentzian-shaped frequency spectrum. These predictions were substantiated by Arecchi *et al.* [58] using polystyrene spheres in water and by Dubin *et al.* [59] using biological macromolecules. Hinds and Reist [60, 61] were the first to apply a laser Doppler spectroscopy (LDS) technique to aerosols, and showed that it worked satisfactorily as an aerosol sizing technique, and that it was equivalent to the earlier work on hydrosols.

When aerosol particles move in the monochromatic illumination from a laser, a whole spectrum of Doppler frequencies is produced due to the velocity distribution of the particles. Frequency shifts of up to a few kilohertz are produced and when this is compared with the typical laser frequency of about $10^{14}$ Hz one is immediately impressed that instruments with the required degree of resolution actually work! In Hinds and Reist's spectroscope the beating together of component frequencies in the scattered light was used so that frequency translation of the spectrum to "zero frequency" occurred. In this "homodyne" system the translated spectrum is twice as wide as the original. A schematic diagram of the apparatus used and a typical Lorentzian response curve is shown in Fig. 11. The frequency response of the electronic equipment was flat to 45 kHz. The experimental technique consisted of selecting about ten sampling frequencies for a period of 15 sec and also at 45 kHz so that an estimate of system shot noise was obtained. After repeating measurements several times the data were then fitted to a Lorentzian curve by a least-squares method and the curve half width at half height was measured. Particle size was then found from theoretical curves relating half width to particle diameter for various angles of scattering.

Hinds and Reist tested their system using aerosols generated by both a modified Weinstock-Rapaport condensation generator and a Collison air-blast system. Reference measurements of particle size were made using Higher Order Tyndall Spectra (HOTS) and polarization of scattered light. Using a dibutylpthalate aerosol the HOTS measurements indicated a particle size of 0.34 μm and the polarization measurement indicated a size of 0.33 μm. The Doppler-shift method indicated a size of 0.35 μm. Other checks and comparisons were made and the particle size measurement by the Doppler method was always close to that predicted by the other methods of measurement. Hinds and Reist estimate that the combined error due to frequency and spectral distortion and noise causes less than a 5% error in determination of the half width of the frequency response curve.

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