Measured Light-Scattering Properties of Individual Aerosol Particles Compared to Mie Scattering Theory

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Monodispersed spherical aerosols of 0.26–2-μ diameter with approximate range of indexes of refraction of atmospheric aerosols have been produced in the laboratory by atomization of liquids with a vibrating capillary. Integrated light scattered 8 through 38 degrees from the direction of forward scattering has been measured with a photoelectric particle counter and compared to Mie theory calculations for particles with complex indexes of refraction 1.4033–0i, 1.592–0i, 1.67–0.26i, and 1.65–0.069i. The agreement is good. The calculations take into account the particle counter white light illumination with color temperature 3300 K, the optical system geometry, and the phototube spectral sensitivity. It is shown that for aerosol particles of unknown index of refraction the particle counter size resolution is poor for particle size greater than 0.5μ, but good for particles in the 0.26–0.5-μ size range.

Introduction

Light-scattering aerosol counters have long been used for aerosol measurement. However, determination of particle size from the counter response for single particles is difficult because of the complicated dependence of the response on particle size, particle index of refraction, lens geometry of the counter optical system, and phototube spectral sensitivity. Although the main purpose of this research was to provide experimental and theoretical results for the response of a particular counter developed in this laboratory for use in stratospheric research, the basic nature of the results for a number of different substances (different indexes of refraction) comprise an interesting comparison of experiment and Mie scattering theory. Other measurements of light scattered by individual particles have been done by Blau *et al.*[1] for transparent spheres 7.5–110 μ in diameter; by Fahlen and Bryant[2] for water droplets 0.6–1.5 mm in diameter; and by Gucker and Egan[3] for transparent spheres 1.4–3 μ in diameter. In this work light scattered by transparent and absorbing spheres 0.26–2 μ has been measured.

Generation of Monodisperse Aerosols

In order to compare Mie scattering theory and experiment adequately, one must be able to generate aerosol particles of arbitrary uniform size and composition. Monodisperse aerosols have been generated by the method of atomization of liquids using a vibrating capillary by Dimmock,[4] Mason and Brownscombe,[5] Ström,[6] and others. However, these efforts have not produced an aerosol of less than 1 μ in diameter. With the technique described here, monodisperse aerosols of 0.26–2 μ in diameter have been generated.

The material to be made into aerosol is dissolved in a volatile solvent; in this work water, carbon tetrachloride, acetone, and alcohol have been used. The solution thus made is forced at high pressure through a small orifice made from glass tubing. The solution must be filtered to prevent particulate matter from clogging the orifice. A transducer is attached to the orifice and at certain resonant frequencies the jet of solution squirting through the orifice breaks under the action of surface tension into spherical droplets of uniform size. The theory for a disintegrating jet of liquid was developed first by Rayleigh,[7] and expanded by Goren,[8] Lindblad and Schneider,[9] and others. It is necessary to disperse the stream of droplets formed by the jet, which are spaced by only about a droplet diameter, to prevent coalescence. This is accomplished by focusing a jet of air perpendicular to the stream of droplets at about a millimeter from the orifice. Using this technique, less than 10% of the droplets coalesce. The volatile component of the droplets evaporates, leaving the residual aerosol. Aerosol less than about 1 μ in diameter coagulates, apparently because the particles are slightly charged and their masses are small enough for electrostatic forces to be important.

The problem of particle coagulation has been greatly reduced by insertion of a gamma-ray source in the tank in which aerosol is made during the time

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of aerosol generation. The gamma rays ionize molecules in the air, which in turn discharge the aerosol. For a 1-m^2 tank, a 0.5-mCi Co^{60} source generally reduces particle coagulation so that less than 10% of the particles coagulate.

The size of the aerosol made with this generator depends on the concentration of material in solution, orifice hole size, orifice pressure, viscosity of the solvent used, and resonant frequency. For example, 40 parts per million Flowmaster ink dissolved in carbon tetrachloride forced through a 5-μ orifice at 60 psi results in a resonance at 510 kHz and generation of aerosol of 0.38 μ in diameter following evaporation of the solvent. An aerosol particle is generated for each complete vibration of the orifice. Obviously the solvent used must be pure. Solvents used in this work were pure to between 1 and 6 parts per million residue.

Monodisperse aerosols have been made of sodium chloride, potassium sulfate, ammonium sulfate, silver nitrate, Dow Corning 200 fluid, and Rhodamin B biological stain. Monodisperse aerosols spherical to within error of measurement by electron microscope have been made of nigrosin dye, Flowmaster ink, potassium dichromate, and polystyrene latex made by Dow Chemical. The aerosol is monodisperse to the extent that the ratio of standard deviation to particle diameter is in the range 0.01 to 0.02, not counting particles that coalesce, forming particles two, three, and four times larger in volume.

Measurement of Aerosol Indexes of Refraction

The indexes of refraction of nonabsorbing aerosols (indexes with zero imaginary part) generated here are known to three and four decimal places and were therefore not measured. The indexes of refraction of nigrosin dye (m = 1.67–0.26i) and Flowmaster ink residue (m = 1.65–0.069i) were measured in bulk form in this laboratory for 6328-Å light to within 2% for the real part and 5% for the imaginary part. Because the materials are highly absorptive, determination of the refractive index real part was done by measurement of intensity of light reflected from a smooth surface of the material. The portion of light reflected at near-normal incidence is related to the refractive index.[10] The imaginary part of the refractive index represents absorption and was determined by measurement of the portion of light transmitted through a dilute solution of the material. A 1-μ layer of nigrosin dye transmits only about 0.15% of light incident normal to the layer.

The Particle Counter

A schematic of the photoelectric counter designed and built by Rosen[11] of this laboratory for balloon-borne stratospheric work is shown in Fig. 1. The instrument is essentially a dark-field microscope with photomultipliers used as the detectors. Air, containing aerosol being sampled, is directed in a well-defined stream through the focal point of the condenser lens, where individual aerosol particles scatter light into the microscopes and photomultipliers. The optical system permits collection of light scattered 8 through 38 degrees from the direction of forward scattering, with a maximum collection efficiency at about 25 degrees.

The output of the photomultipliers is a measure of intensity of light scattered by single particles, but also depends on the spectrum of light incident $E(\lambda)$ and the photomultiplier spectral sensitivity $S(\lambda)$. The output of one photomultiplier is fed into a 400-channel pulse-height analyzer; the other is used for coincidence.

A typical spectrum, counts vs channel number for

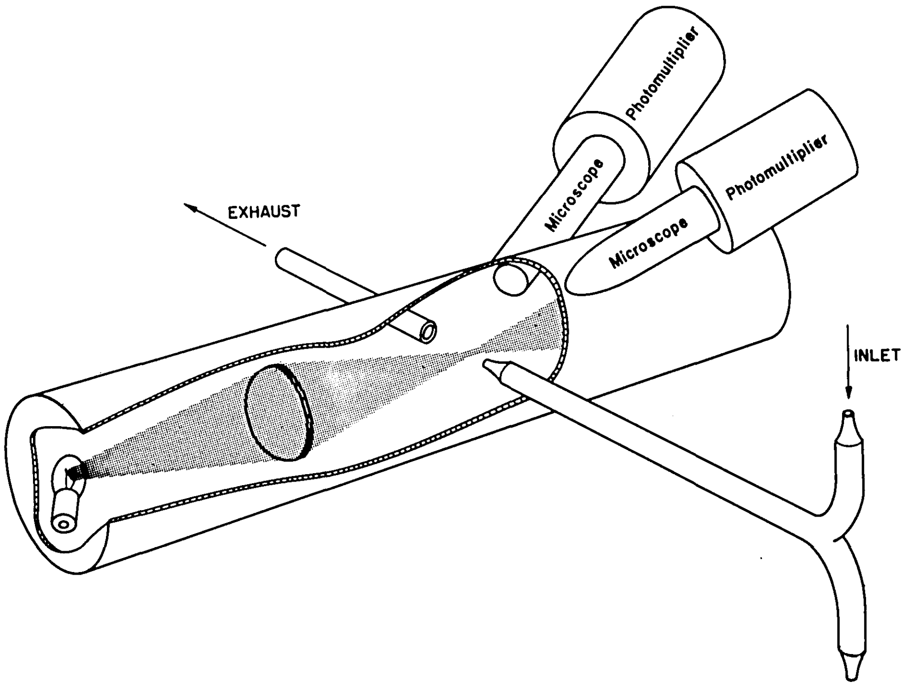

Fig. 1. A schematic diagram of the photoelectric particle counter.

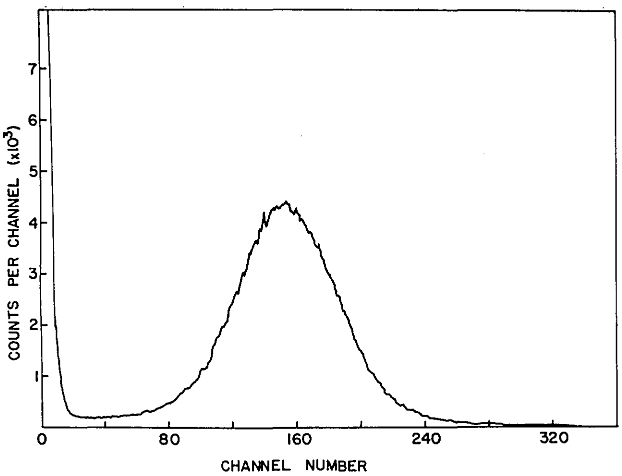

Fig. 2. A typical pulse-height analyzer spectrum for monodisperse aerosol.

monodisperse aerosol, is shown in Fig. 2. This particular spectrum is for 0.74-μ-diameter Flowmaster ink aerosol and the peak at channel 152 corresponds to that size. The position of the peak is a measure of the average intensity of light scattered by an aerosol particle and is proportional to the counter response. The counter response to this aerosol is 48 photoelectrons per particle. The spread in the peak, in decreasing order of significance, is due to photoelectron statistics, the fact that not all the aerosol particles pass the field of view of the microscope in the same time and moreover that all aerosol is not uniformly illuminated, and variation in aerosol size. The steep edge in the spectrum at about channel 15 is due to Rayleigh scattering from molecules of the air and ultimately limits the sensitivity of the instrument.

Calculation of Intensity of Scattered Light and Particle Counter Response

If unpolarized light of intensity I_0 and wavenumber k is incident on a homogeneous sphere of radius r and index of refraction m, the intensity of scattered light at a point with coordinates (R,θ) is, according to Mie theory,[12]

$$I(R,\theta) = I_0\{[i_1(x,m,\theta) + i_2(x,m,\theta)]/2k^2R^2\},$$

where x is the size parameter, $x = 2\pi r/\lambda$, θ is the angle measured from the forward scattering direction, and λ is the wavelength of incident light. The dimensionless quantities i_1 and i_2 are associated with intensity of light scattered with electric vector parallel and perpendicular to the plane of scattering. They consist of squares of infinite series of terms that are functions of spherical Bessel functions, Legendre functions, and their derivatives. In this work they were computed with a subroutine written by Dave.[13]

For the photoelectric counter considered here the light reaching the detector is not monochromatic and comes from a range of scattering angles. Therefore the counter response to a particle includes integration of i_1 and i_2 over a white light spectrum $E(\lambda)$ and over the angular interval 8–38° properly weighted. The spectral sensitivity of the photomultiplier $S(\lambda)$ must also be folded into the calculation. Thus the response of the counter to a single particle is proportional to

$$\int_{8°}^{38°} d\theta \int_0^\infty d\lambda \left(\frac{\lambda}{2\pi}\right)^2 \left[i_1(x,m,\theta) + i_2(x,m,\theta)\right] E(\lambda)S(\lambda)f(\theta).$$

The quantity $f(\theta)$ depends on the angles subtended by the focusing and collecting lenses of the counter optical system. It is a measure of the light collection efficiency as a function of angle from forward scattering and is a smoothly varying function peaked at about 25°. Graphs of $E(\lambda)$ for color temperature 3300 K and $S(\lambda)$ for the EMI 9524S photomultiplier tubes used here are shown in Fig. 3. The spectral sensitivity, or quantum efficiency, is shown as photoelectrons per photon in percent. The calculation of the counter response is not absolute, and so must be normalized to measurements for comparison. A calculation similar to the one described here has been carried out by Quenzel.[14]

Comparison of Experiment and Theory

Measurement of the counter response for spherical monodisperse aerosol of nigrosin dye (m = 1.67–0.26i), Flowmaster ink (m = 1.65–0.069i), Dow Corning 200 fluid (m = 1.4033–0i), and polystyrene latex (m = 1.592–0i) are shown in Figs. 4 and 5 as circles and triangles. All diameters except for Dow Corning 200 fluid were determined by electron microscope. The response is expressed in average photoelectrons per particle generated at the photomultiplier photocathode and is related directly to the pho-

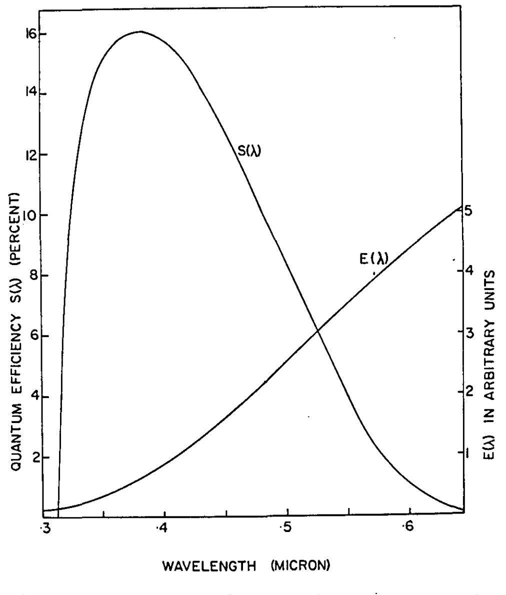

Fig. 3. Quantum efficiency $S(\lambda)$ for the EMI 9524S photomultiplier tube and blackbody spectrum $E(\lambda)$ for color temperature 3300 K. Ordinate scale for $E(\lambda)$ is arbitrary.

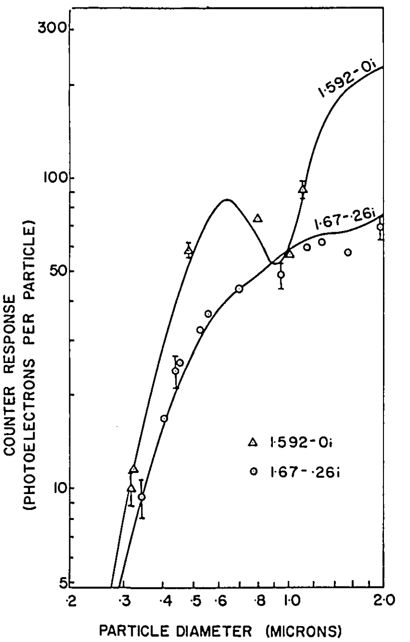

Fig. 4. Photoelectric particle counter response; measured *(circles and triangles)* and calculated using Mie scattering theory *(smooth curves)* for single particles vs particle size. Calculated curves have been normalized for best fit the measured response for polystyrene latex particles with refractive index $m = 1.592–0i$.

tons scattered per particle through the quantum efficiency $S(\lambda)$ shown in Fig. 3. The smooth curves are computer-calculated theoretical results and have been normalized for best fit to the measured response for polystyrene latex aerosols. This normalization was used for all theoretical results presented here. Error in measurement of response is primarily from variation in photomultiplier tube gain; error from photoelectron statistics is negligible because each data point represents about 10^5 particles counted. The response error bars for nigrosin are largest because those data were taken using a photomultiplier high voltage power supply less stable than the one used for all the other data shown.

The error in measurement of diameter for polystyrene spheres is much less than the width of the triangles marking the measurements. The standard deviations in particle size are 59 Å or less as measured by Dow Chemical. The error in measurement of nigrosin dye and Flowmaster ink particle diameters is 5%, or about the width of the circles marking the measurements in Figs. 4 and 5. It should be mentioned that the error in measurement of the nigrosin dye and Flowmaster ink indexes of refraction causes differences in the calculated response curves of as much as 10% for a given diameter from the curves shown. The particle diameters of aerosol made from Dow Corning 200 fluid were not measured directly because of its high volatility at electron microscope pressure and temperature. These aerosols were made with the same solvent, orifice, orifice pressure, and resonant frequency as the Flowmaster ink aerosols. The particle diameters were then calculated from the ink particle diameters taking into account concentration of ink and 200 fluid in solution and the material densities. Hence the error in 200 fluid particle diameters is larger than that for the ink because of error in measurement of material densities. It is assumed, of course, that 200 fluid aerosol is spherical. The resulting error in 200 fluid aerosol diameters is 9%, or twice the width of the triangles marking the measurements.

Conclusions

The measured response and the response calculated with Mie scattering theory are in general agreement within errors of measurement. In particular the measurements on polystyrene latex aerosols, for which the index of refraction is known to four decimal places and particle diameter to 59 Å or better standard deviation, compare closely to the calculated response. Therefore a measure of confidence can be placed in response curves calculated for materials with indexes of refraction different from those studied here.

A few measurements of the counter response for slightly nonspherical, randomly oriented particles of size about 0.5 μ and smaller (measurements not shown here) agree with the Mie calculated response for spheres of equal volume and refractive index. This result supports that of Holland and Gagne,[15] who found that for a polydisperse, randomly oriented, nonspherical system of particles 0.15–1.5 μ in size the unpolarized mass scattering coefficient is ap-

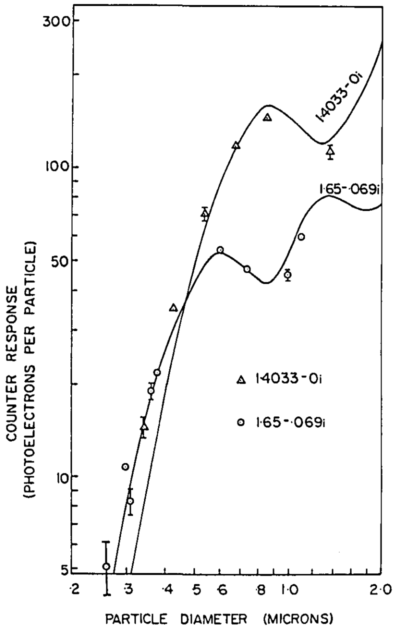

Fig. 5. Photoelectric particle counter response; measured *(circles and triangles)* and calculated using Mie scattering theory *(smooth curves)*, for single particles vs particle size. Calculated curves have been normalized for best fit to the measured response for polystyrene latex particles with refractive index $m = 1.592–0i$ (see Fig. 4).

proximately that for spherical particles for scattering angles less than 40 degrees from the direction of forward scattering.

Further conclusions concerning the particle counter derived from this study are the following. If the counter is used to size aerosol of unknown index of refraction, it clearly has a poor size resolution for particles of diameter larger than 0.5 μ. For example, a particle 0.55 μ in diameter with index 1.592-0i gives the same response as a particle 1.8 μ in diameter with index 1.67-0.26i. Even for particles of a given index the size resolution is not good above 0.5 μ in diameter, as there is not always a unique relationship between counter response and particle size. However, the counter size resolution is good for particles less than 0.5 μ in diameter, even for the large range in refractive index studied here.

The ultimate lower size limit of sensitivity of the particle counter is approximately 0.26-0.30 μ in diameter, depending on particle index of refraction. For these smaller particles, the instrument efficiency decreases, since the spectrum of scattered photons becomes a broad Poissonian due to the fact that the average photoelectron count per particle is only about 5. The light pulses from about half of the particles are not counted because they fall below the light pulse level of Rayleigh scattering from molecules of the air. Scattering chamber evacuation and increased light source intensity will not help in lowering the size limit appreciably, since the particle scattering response falls off as r^6 in this size region.

The range of indexes of refraction of atmospheric aerosols is nearly bracketed by that of aerosols studied here, so the counter can be used to give a rough indication of atmospheric aerosol size distribution, especially for particles with diameters in the 0.26-0.5 μ range, where the counter resolution is good and effects of particle nonsphericity are small.

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O. WOLCOTT GIBBS

1822–1908

Considered by Agassiz "the first chemist of the nation" Wolcott Gibbs was drawn into the Lazzaroni circle as a result of his steadfast commitment to the ideal of professionalism (see page A14). Gibbs was educated at Columbia, the College of Physicians and Surgeons in New York, and in Europe. After fourteen years as a professor in the College of the City of New York, he accepted, at the urgings of Peirce and Agassiz who wished to see science elevated at Harvard, the Rumford Professorship in chemistry and the Deanship of the Lawrence Scientific School, much to the chagrin of Charles W. Eliot who had hoped to occupy that renowned chair. Later, Gibbs became active in the National Academy of Sciences, serving as its president from 1895 to 1900.