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LIGHT SCATTERING BY VERY DENSE DISPERSIONS

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ABSTRACT

The scattering of light by very dense dispersions has been investigated. Attention has been directed to dispersions in which the mean distance between particles is only a few particle diameters. At these distances, the particle fields are known to interact, and hence the scattering cannot be described in terms of single-particle scattering. No experimental data have previously been reported for this phenomenon.

The use of spherical particles about a centimeter in diameter and high-frequency radio waves was investigated, since the scattering would be analogous to light scattering at the same index of refraction and the same wavelength to diameter ratio. However, the complexity and cost of the necessary equipment were found to be prohibitive.

Deduction of interaction from light transmission was found to be feasible although extremely precise measurements are required. Equipment for measurement of the transmission of monochromatic light in the visible range through very dense monodispersions of latex particles has been developed, constructed and calibrated. Exploratory data have been obtained.

The investigation is being continued under the sponsorship of the Department of Chemical and Metallurgical Engineering of the University of Michigan.

LIGHT SCATTERING BY VERY DENSE DISPERSIONS

INTRODUCTION

In 1908, Mie (6) derived rigorous equations describing the scattering of electromagnetic radiation by spherical particles. During recent years, Mie's solution has been applied to many practical problems. Most of this work has been directed toward the determination of the particle-size distribution and the specific surface of dispersions, such as clouds, fogs, sprays, emulsions, etc. Mie's solutions have also been used for the determination of the molecular weight of polymers.

In all these cases the concentration of particles is relatively dilute, i.e., the distance between particles is large in comparison with the particle diameter and the wavelength of the incident radiation. Hence, the scattering properties of the individual particles are completely defined by the particle diameter, the wavelength of the incident radiation, and the relative index of refraction of the particles and the surrounding media. The scattering properties of a dispersion are then defined by the scattering properties of a single particle, and the total number of particles per unit cross section.

The scattering also becomes dependent upon the mean distance between particles when this distance is reduced to the order of a few particle diameters. This change is due to the effect of the electromagnetic field of one particle upon an adjacent one. For concentrations such that this interaction is important, the equations developed by Mie are no longer applicable. The mean distance at which interaction becomes important is not known. Sinclair (8) states qualitatively that this interaction would be expected to occur when the particles are less than ten radii apart. The objective of this investigation is to describe scattering by such dense dispersions.

A knowledge of light-scattering by very dense dispersions is important in many applications. Interaction may be important in radiant heat transfer through fibrous insulations. In simulation of atmospheric dispersions by dense solid-in-liquid dispersions (7) interaction may be encountered. Lastly, in the limit when the particles become contiguous, the dispersion can be considered as a surface and insight may be gained into the optical relationship between a dispersion and a surface.

Before considering possible methods of investigation of this problem, it is advantageous to anticipate some of the results. It is difficult to predict the exact variation in angular distribution due to electromagnetic interaction; however, certain deductions are possible concerning the total amount of energy scattered by a single particle in a dense dispersion. This total amount of energy scattered by a particle is usually expressed in terms of an effective cross section for scattering. If two spheres are separated by a large distance and placed in a plane-polarized electromagnetic field they behave as individuals and the total scattering cross section is the sum of the two scattering cross sections. As the particles approach one another, their fields begin to interact, and it would be expected that the total amount of energy scattered would decrease. This type of phenomenon has been observed in the case of molecular scattering by water (10). The scattering of light by molecules of a gas can be predicted theoretically when the distance between molecules is relatively large. The mean free path of a photon can then be calculated. These calculations have been verified experimentally. When the same theory is applied to liquid water where the distance between molecules is small, a mean free path of about 200 meters is predicted but a mean free path of about 1000 meters is observed. Thus, the effective scattering cross section is apparently decreased due to the close proximity of the water molecules.

METHODS OF SOLUTION

Various theoretical and experimental approaches are possible. Several methods are discussed below.

Theoretical Methods

Mie solved the problem of scattering of plane-polarized electromagnetic radiation by a single spherical particle by integration of the Maxwell equations for the appropriate boundary conditions. It appears at least remotely possible to solve the Maxwell equations for a two-sphere system. However, the Mie solution, itself, is an exceedingly complex series which converges very slowly. A two-sphere solution would certainly be an order of magnitude more difficult. The interaction of the two fields is a function of the orientation of the spheres with respect to the incident radiation, i.e., a two-sphere system must be allowed three degrees of freedom, 2 rotational (angles with the axis of the spheres and the incident plane-polarized radiation) and 1 translational (distance between particles). This introduces three additional variables into the solution. The geometry of such a system is exceedingly complex and cannot readily be handled by any of the common co-ordinate systems. All in all, an exact solution does not appear to be feasible.

In principle, it is possible to calculate the modification of the electromagnetic field at a point due to the close proximity of other particles by utilization of a method similar to that of Born (1). To utilize this modified field method, the distribution of energy of the particles under consideration must be known. However, the distribution is generally so complex that the method proves very difficult to apply. As the particle size becomes small in comparison to the wavelength, the distribution becomes isotropic and application may be possible.

As the particle diameter becomes very large in comparison with the wavelength of the incident radiation, geometric optics and diffraction theory can be used to calculate the energy scattered by a two-sphere system (5, 9). A few qualitative factors about the application of diffraction theory should be noted. A circular disc in a beam of parallel light yields a diffraction pattern of light and dark rings on a plane situated a large number of wavelengths behind the disc. Two discs, whose distance of separation is large in comparison with the wavelength, yield a pattern which is the sum of the diffraction patterns of the individual discs. As the two discs approach one another until they are only a few wavelengths apart, the diffraction pattern in the central region behind the discs is altered and approaches that of a narrow slit, thus considerably altering the distribution in the central area. Even though the diffraction method is not applicable to small particles, such a study should be helpful in interpreting the effect of interaction.

Experimental Methods

Two quite different experimental techniques appear possible for the determination of the effect of electromagnetic interaction. One involves the use of microwaves, i.e., high frequency radio waves and two spheres. The other involves measurement of the transmission of visible radiation through a dense dispersion of uniformly sized particles. Since the scattering properties of a single particle depend upon the index of refraction and the ratio of the particle diameter to the wavelength of the incident radiation, the results of either study can be interpreted for the other range of wavelengths.

Microwave

Two dielectric spheres could be placed in a collimated beam of plane-polarized radiation and the spatial intensity distribution found by making traverses with an antenna. This type of equipment has been used to determine the effect of particle shape on scattering properties in many light-scattering laboratories. However, for the proposed investigation, several severe restrictions must be placed upon the microwave equipment.

1. The source must emit a collimated beam which is uniform over a diameter of at least 10 wavelengths and preferably 20.

2. The receiver must be nearly collimated so that it receives radiation from only a very small solid angle, preferably less than 0.01 steradian. This is particularly critical in the forward direction where the scattered energy must be distinguished from the transmitted portion of the incident radiation.

3. The receiver response should be linear or at least known over a 10^6 range in input signals since the intensity varies at least this much around a scattering particle.

4. The entire equipment must be surrounded by a material which absorbs the microwaves so that the particles and the receiver do not receive energy from the walls.

Some of these restrictions can be relaxed if attention is limited to particles which are small in comparison with the wavelength. In this case, the distribution is nearly uniform so that the range of operation of the receiver can be reduced considerably.

Some mention should be made of the number of measurements required. A complete spatial intensity distribution in both planes of polarization and a graphical integration over all space would be necessary. The two rotational and the translational variables previously mentioned must be studied independently and thus the number of measurements required for a complete study of only one particle size is extremely high.

After thorough investigation, this method was abandoned because of prohibitive costs and the aforementioned difficulties.

Light Transmission

The transmission method involves passing a collimated monochromatic beam of light through a dispersion of uniformly-sized particles. The light which emerges from the dispersion in the forward direction consists of two parts, the undistrubed portion of the incident beam and scattered light. This transmitted light can be measured by a sensitive detection device as a function of concentration. As the concentration of the particles increases from zero, an exponential decrease of energy is first obtained. This is known as the single scattering range and the energy which a narrow angle receiver detects consists largely of unscattered energy. As the concentration is further increased, the transmission is greater than that predicted from the exponential decay. In this range of concentrations, the energy which is collected by the receiver includes a significant portion of multiply-scattered radiation (2). If the particle concentration is increased still further and interaction effects become appreciable, the transmission is greater than that resulting from multiple-scattering. Transmission measurements with various concentrations, particle sizes, and wavelengths should establish the value of the parameters at which the interaction effects are appreciable and thus establish a practical limit for application of the Mie equations.

It is important that size of the equipment be eliminated as a variable. Thus, when the cell thickness is increased, all of the other dimensions of the system, such as the beam cross section, the cell area, and the receiver cross section, must be increased proportionally. If the dispersion is to approximate a semi-infinite dispersion, the cell walls must be sufficiently removed from the light beam so that they have no effect on the energy collected by the receiver, or the cell walls must have such reflectivity that the same net flux will be passing through the walls as would have passed that plane if the dispersion were infinite, and that the energy which is reflected will have the same distribution as that which would have been present in an infinite bed.

The first of these conditions is the easier to utilize since the necessary reflectivity varies with the particle concentration. If the cell is sufficiently large in cross section with respect to the beam of light, a variation in the size of the cell would not affect the amount of energy detected by the receiver. The size of the receiver would not be critical if the receiver were large enough to intercept the entire cross section of the incident beam. The effects of all these parameters can be easily checked experimentally.

Since multiple scattering and electromagnetic interaction will both be encountered with dense dispersion, it is not to be expected that the effect of interaction will be apparent from a plot of attenuation or transmission versus concentration alone. If only single and multiple scattering are considered, the functional relationship between transmission and concentration can be expressed as

$$\ell n \frac{I_o}{I} = f(nqt) \qquad (1)$$

where I_o = the power of the incident beam
I = the power of the emerging beam
$f(nqt)$ = a function of nqt
n = the number of particles per cc. of suspension
q = the scattering cross section (cm^2)
t = the cell thickness (cm)

For a constant value of nqt the transmission is constant and independent of the concentration of particles. Interaction can thus be distinguished by varying the particle concentration while maintaining a constant value of nqt.

The actual equipment and operating procedure are discussed in the following section.

EXPERIMENTAL EQUIPMENT

The experimental equipment can be divided into three parts:

1. The source and collimating unit,
2. The cells,
3. The receiver.

The overall appearance of the equipment is shown in Figures 1 and 2.

Source and Collimating Unit

An enclosed mercury arc lamp was used as the source because the green line (5460 Å), can easily be isolated to give monochromatic light of high purity. General Electric high pressure mercury arc lamp Model CH-3 was selected because the brightness is higher than the low pressure mercury arcs and the pressure is not high enough to cause too much background around the principle lines. An absorption type Kodak Wratten 77-A filter was selected to isolate the green line. The Wratten 77-A filter transmits 68 percent of the green line and a negligible percentage of the yellow lines. The red lines of the mercury spectrum have a negligible effect even though they are transmitted by the Wratten 77-A filter since the photomultiplier used as a receiver has a very small sensitivity to the red.

A collimated beam of light was obtained by the use of an effective point source. The schematic arrangement of the optical system is shown in Figure 3. The parts are mounted on optical benches. The energy emitted by the CH-3 is condensed by condensing lenses L_1 and L_2 into the pinhole P_1 after passing through the Wratten 77-A filter F. The Iris diaphrams D_1 and D_2 are used to diminish the amount of unwanted radiation from reaching the collimating lens. The shutter S_1 is placed next to the pinhole P_1 and the pinhole is placed at the focal point of the collimating lens L_3. The collimating lens is an achromatic, coated telescope objective, 52 mm in diameter and 192 mm in focal length. D_3 is a diaphram in front of the collimating lens and is used to limit the diameter of the collimated beam. The inside of the collimating

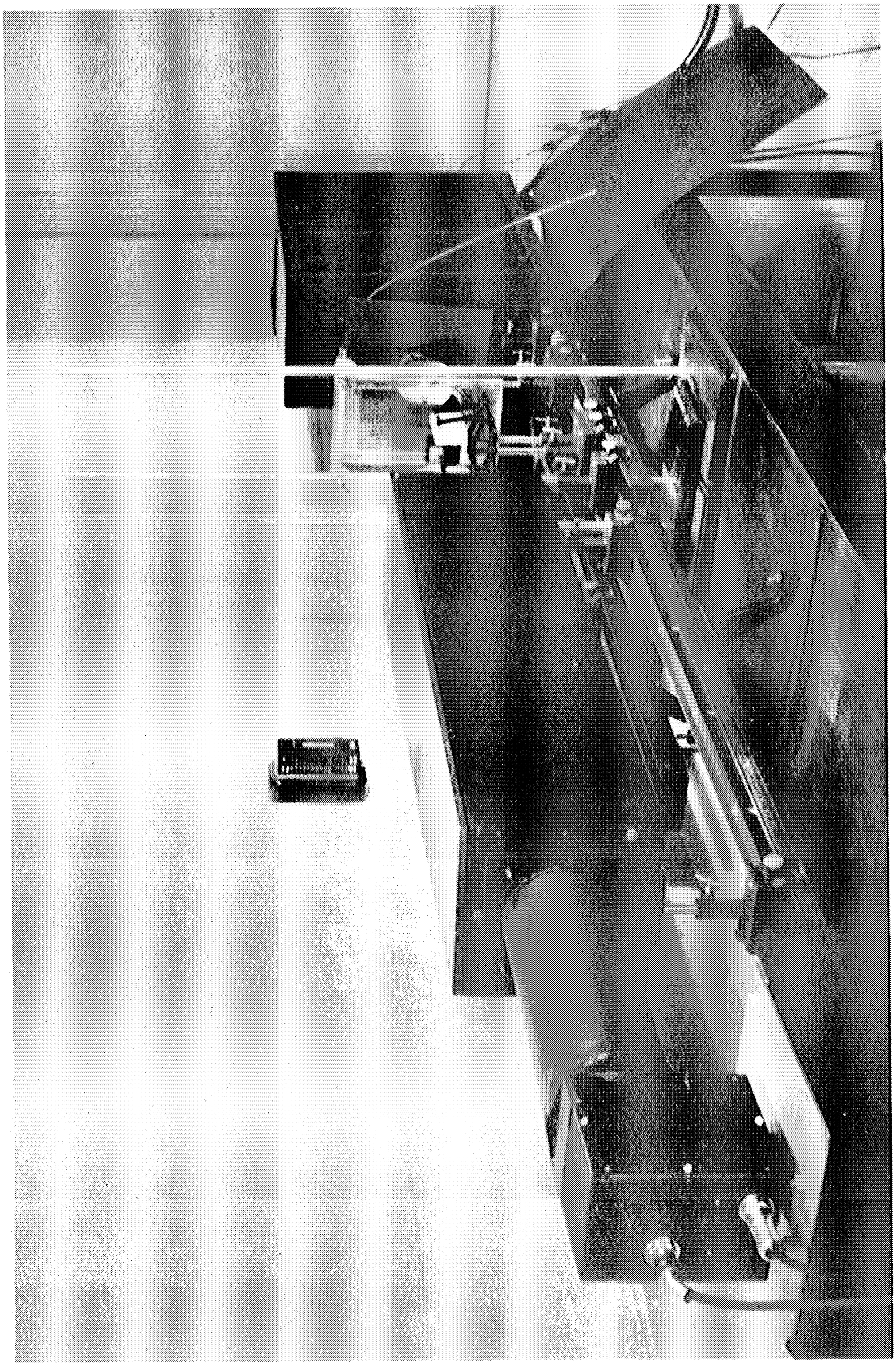

Figure 1. Photograph of equipment.

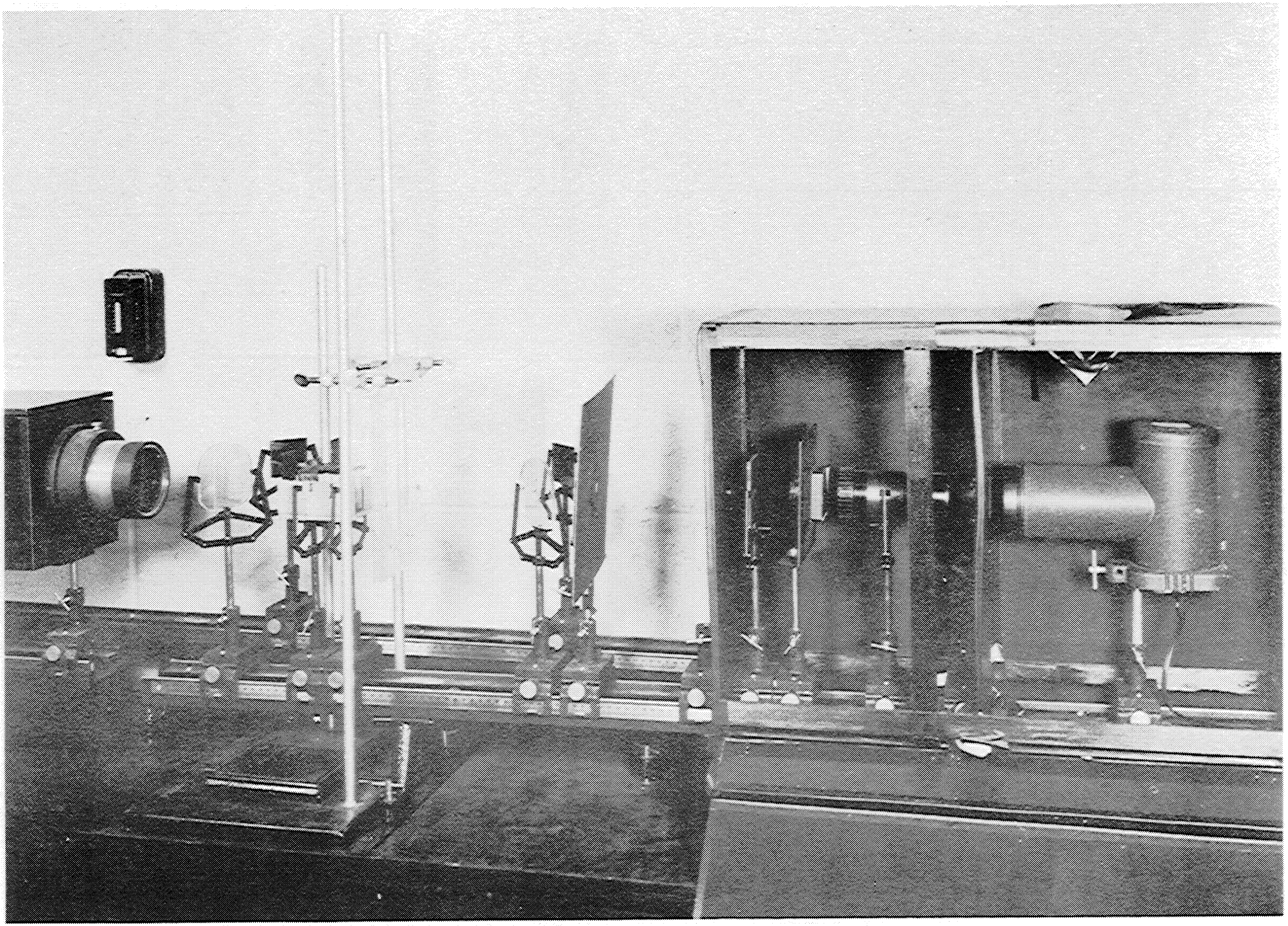

Figure 2. Photograph of source and cell.

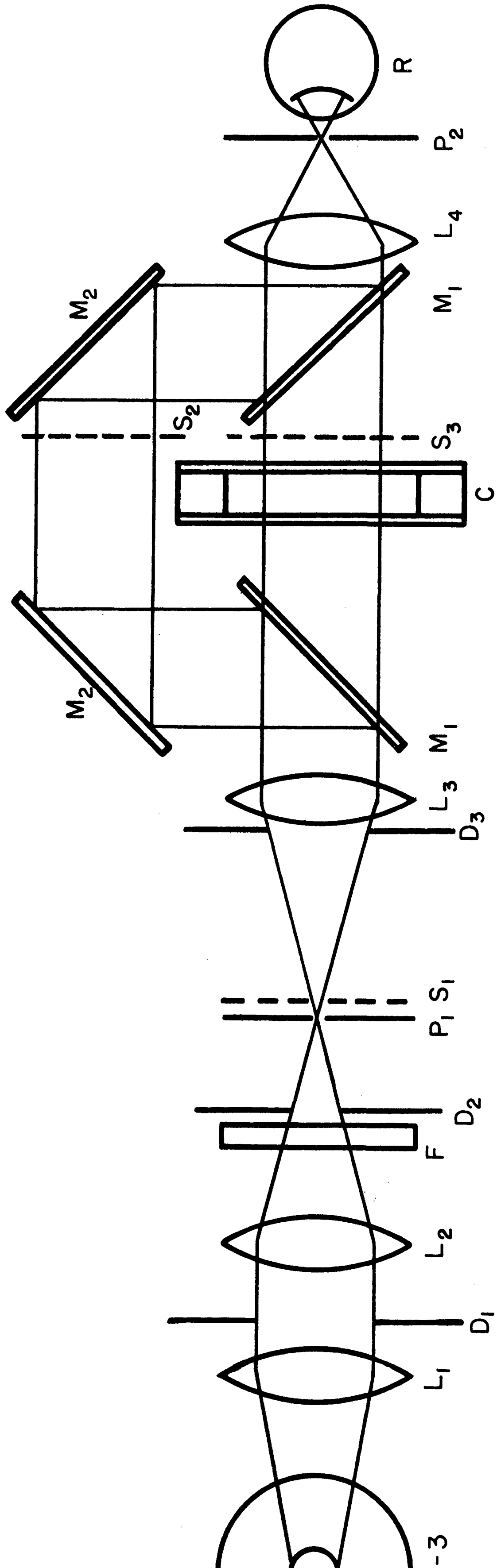

Figure 3. Schematic diagram of optical equipment.

unit is blackened to minimize reflection and scattering. A small darkroom blower is used to supply air for cooling the lamp. With a 1/32-inch pinhole and a collimating lens of 192 mm focal length the divergence of the parallel beam is 7.1 minutes.

Dispersion Cells

The dispersion cells are constructed from Plexiglas and are shown in Figure 4. The bottom is semicircular to insure uniform mixing when particles are added and to insure that a minimum number of particles will ne necessary for a run. The beam of light will be passed through the center of this semicircle. Six cells were constructed of varying thickness. The thickness was measured in a number of positions around the perimeter of each cell. The average values for the six cells are 0.167, 0.319, 0.447, 0.665, 0.768, and 0.901 inches. Measurements indicate that the cell faces are not out of parallel by more than 30 minutes. The cells were constructed so that the edges are far enough away so that they should have no effect on the transmission through dense dispersions. Larger cells will be constructed to confirm this assumption.

The Receiving and Measuring Unit

A camera is placed behind the dispersion cell to collect the light. The camera body (7 inches x 7 1/2 inches x 33 3/16 inches) is a wooden box painted flat black. The front of the camera box is fitted with a lens holder with fine threads for focusing. The camera lens is an achromatic, coated telescope objective--83 mm in diameter and 914 mm in focal length. At the back of the camera and at the focal point of the receiving lens a pinhole P_2 is placed. There is no shutter on the camera since it is placed at the source unit. If a 1/4-inch pinhole is used on the receiver the reception angle is 11.7 minutes.

The radiation is collected by a photomultiplier placed about 350 mm behind the pinhole. The photomultiplier is housed in a light-tight metal box and a light-tight tube is used to transmit the light to the photomultiplier. The inside of the box and tube are painted flat black. The photomultiplier is a RCA 931-A nine stage tube and is operated by a Furst Electronics Model 710-PR 300 to 1500 volt variable negative power supply. The circuit diagram for the photomultiplier and the measuring circuit is shown in Figure 5. Three 45-volt "B" batteries are used in series to provide the voltage between the ninth dynode and the anode. The anode current is determined by measuring the potential drop across a 1000 or 6000 ohm precision resistor in the anode circuit with a precision potentiometer. Precision resistors with a low temperature coefficient are used in the voltage dropping circuit of the photomultiplier to minimize temperature effects during measurement. The amplification of the

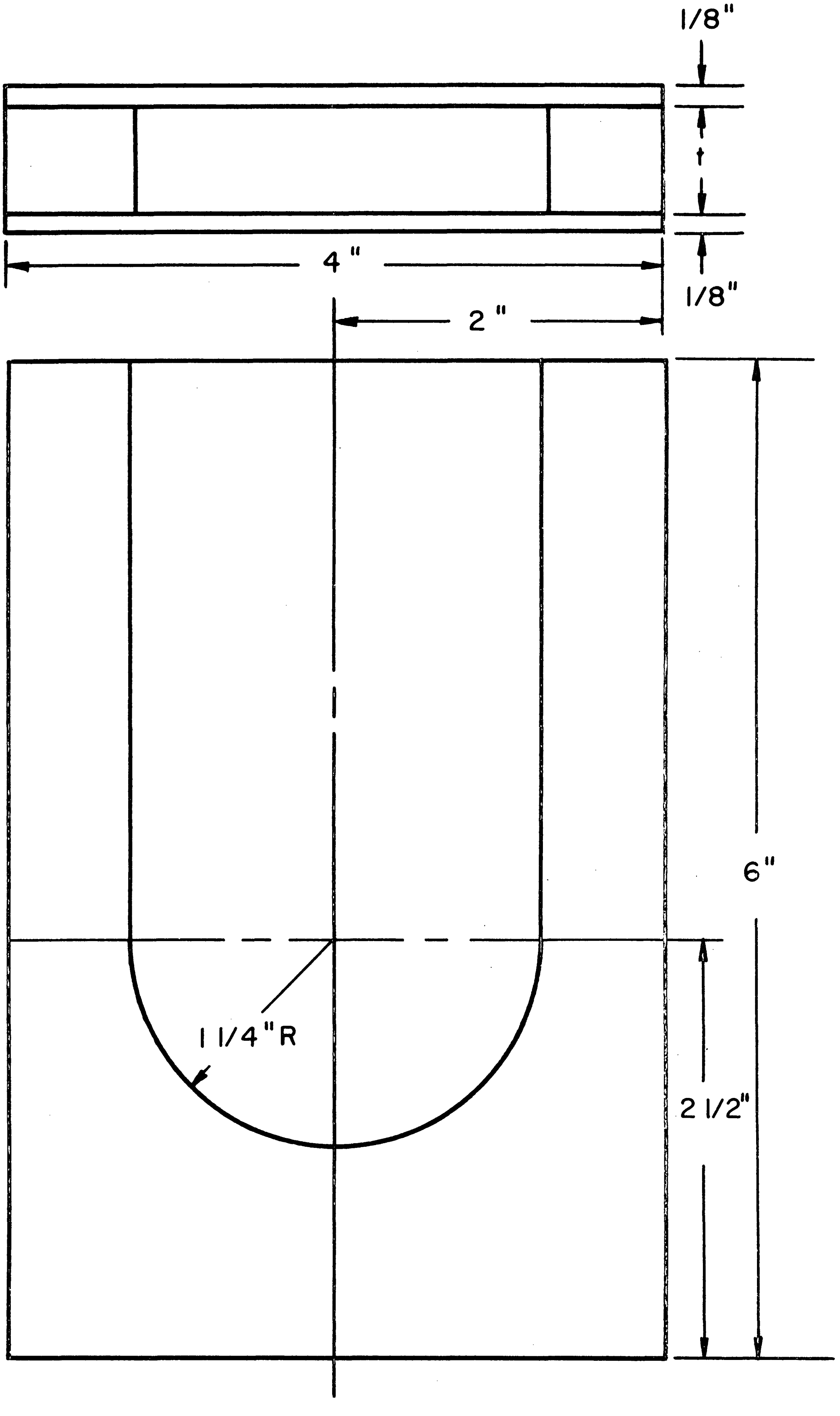

Figure 4. Test cell.

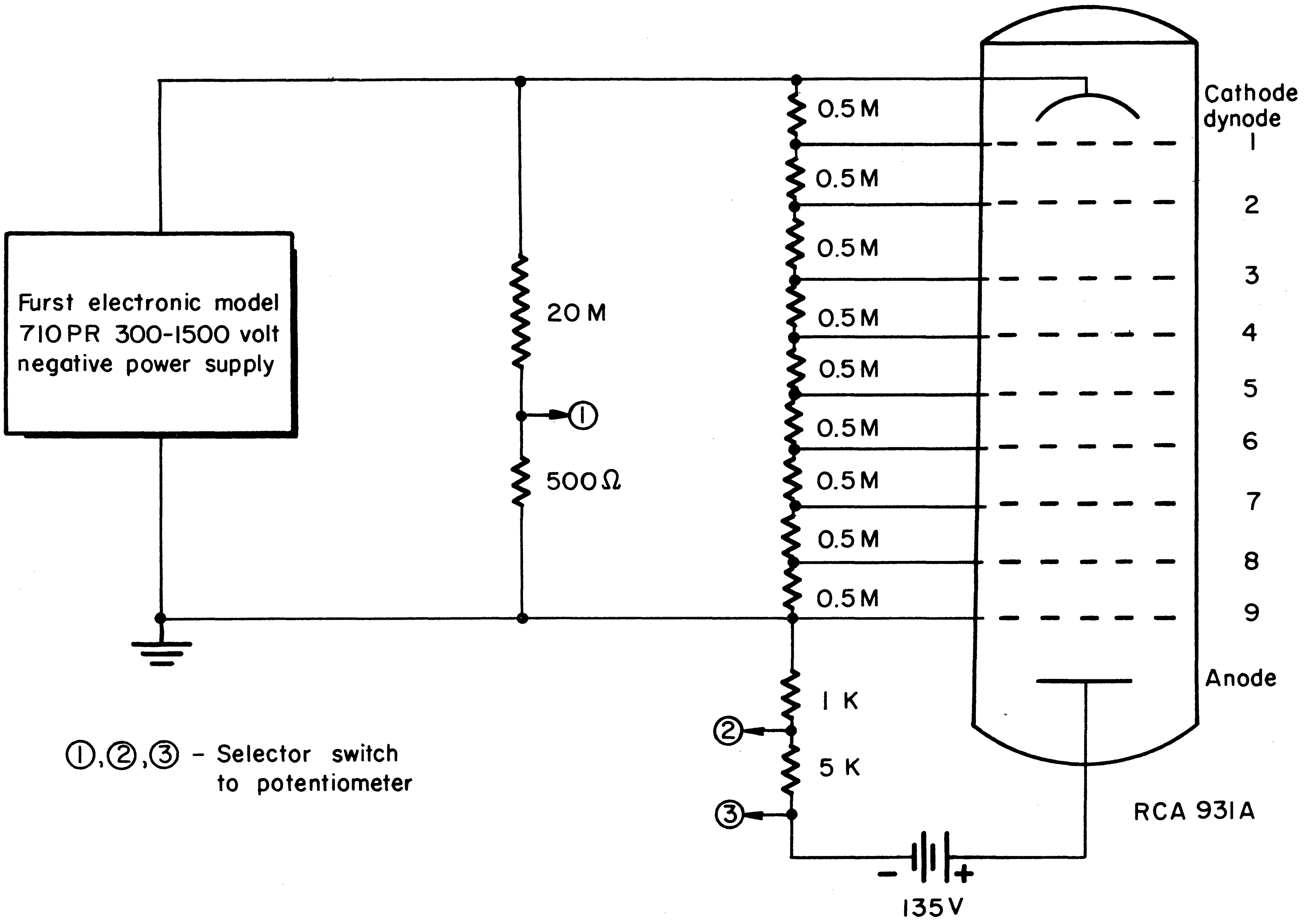

Figure 5. Photomultiplier wiring diagram and measuring circuit.

photomultiplier can be adjusted by charging the dynode voltages. A 20 megohm and a 500 ohm resistor in series were put across the cathode and dynode number 9 so that the cathode supply voltage could be determined accurately by measuring the potential drop across the 500 ohm resistor.

EXPERIMENTAL PROCEDURE

The dispersions to be studied consist of latex spheres of very uniform size supplied by the Dow Chemical Company. These particles are very stable in a water dispersion and have a relative index of refraction of 1.20 with respect to water. Diameters of 0.236 and 0.814 microns will be used initially. Other sizes are available if necessary. The dispersions are available in concentrations of about 40 per cent by weight in water.

During the initial studies to check the equipment certain instabilities were noted. These instabilities are due to both slight variations in the brightness of the lamp and in the voltage applied across the dynodes of the photomultiplier. Due to the high multiplication of electrons at each dynode, a variation of 0.5 per cent in the voltage across the dynodes will cause a significant change in the output signal. Because of these variations in signal, a monitor beam consisting of a bypass for the light beam around the cell was established so that a reference signal could be used to reduce all the transmission measurements to a common basis. The bypass is shown in Figures 2 and 3. A half-silvered mirror M_1 is placed between the collimating lens and the cell at an angle of 45° to the original beam (see Figures 2 and 3). The energy reflected from this mirror is then reflected by a first-surface mirror M_2 into a path which bypasses the cell parallel to the original beam. This beam is then reflected to the camera by a first-surface mirror and a half-silvered mirror. The shutters S_2 and S_3 are used to select the beam which is to be measured.

A small portion of the output signal is due to a small current flow known as a "dark current". This current flows even though there is no light falling on the photocathode and is due to the thermionic emission, ionization, ohmic leakage, etc. (3). The value of the dark current is measured after each signal and subtracted from the original measurement.

The alignment of the equipment is particularly critical. To obtain an accurate knowledge of the transmission, it is necessary that the beams converge at the center of the pinhole of the receiver. The equipment is, therefore, carefully aligned before each run using a system of crosshairs at the pinhole.

A firm knowledge of the concentration of the particles in the original stock solution is necessary. This concentration is determined optically in the same equipment described in the previous section. If the experimental study is restricted to relatively dilute dispersions the transmission can be represented by the equation

$$\ell n \left(\frac{I_o}{I}\right) = nqt \tag{2}$$

Equation 2 can be rewritten in terms of the amount of concentrated stock solution added as

$$\ell n \left(\frac{I_o}{I}\right) = \left(\frac{V_s}{V_s + V_w}\right) Nqt \tag{3}$$

where V_s = the total volume of stock solution added
V_w = the volume of distilled water initially present
N = the number of particles per cm^3 of the stock solution

Equations 2 and 3 are valid only when the value of nqt is less than 1.0. To determine the concentration the stock solution is volumetrically diluted to a convenient concentration and then is added to a cell which contains a known volume of distilled water. The signal due to the transmitted beam is measured for the water and after each addition as well as the signal due to the minitor beam and the dark current. From this data and Equation 3, the value of Nqt can then be determined. The thickness of the cell is known. The value of q can be determined from available tables (4) as a function of the particle diameter, wavelength, index of refraction. The value of N can then be calculated.

For the actual runs, a known volume of distilled water first is placed in the cell and the transmission determined as before. This transmission serves as the I_o measurement, and the value of the monitor signal serves as a reference. The stock solution of particles is then added incrementally and the transmission, monitor signal, and dark current measured after each addition. The transmission minus the dark current is then corrected to the original value of the monitor signal. When the signals get too small for accurate measurement the amplification is increased by increasing the dynode voltages. The monitor signal is decreased to a value which can be measured by the potentiometer by placing neutral density filters in the beam. The data is corrected to the original amplification (dynode voltages) by using the amplification factor determined by the monitor and the transmission. This data is then plotted versus the volume of stock solution added divided by the total volume of liquid present, in order to check for consistency. This type of data will be taken for cells of various thicknesses.

EXPERIMENTAL WORK

To date quantitative measurements have been limited to dilute dispersions. These dilute dispersions were tested to check the operation of the equipment. The data were taken with a cell which is slightly larger than the one shown in Figure 4 in size. The inside dimensions are 4 inches in width by 8 inches maximum depth by 0.26 inches thick. Test data with a dilute dispersion of particles 0.814 microns in diameter are given in Table 1 and the points are shown on Figure 6. The dark current has been subtracted from the readings presented in Table 1. In the table, e represents a signal which is proportional to the amount of light transmitted through the cell and the dispersion, and e_M represents the signal proportional to the amount of light in the monitor beam. e_c is the corrected value of e when it is reduced to the original value of e_M. The value of Nq determined from this run was 2.729 with an average deviation of 1 per cent giving a particle concentration of 3.099×10^8 per cc. These data have been duplicated on other successive runs.

CONCLUSIONS

Direct information on the interaction between particle fields might be obtained from the scattering of high frequency radio waves by a two-sphere system but the development and cost of the necessary equipment is beyond the scope of this grant.

The effect of particle interaction can be characterized by the measurement of light transmission through very dense dispersions. The necessary equipment has been developed, calibrated and tested.

ACKNOWLEDGEMENT

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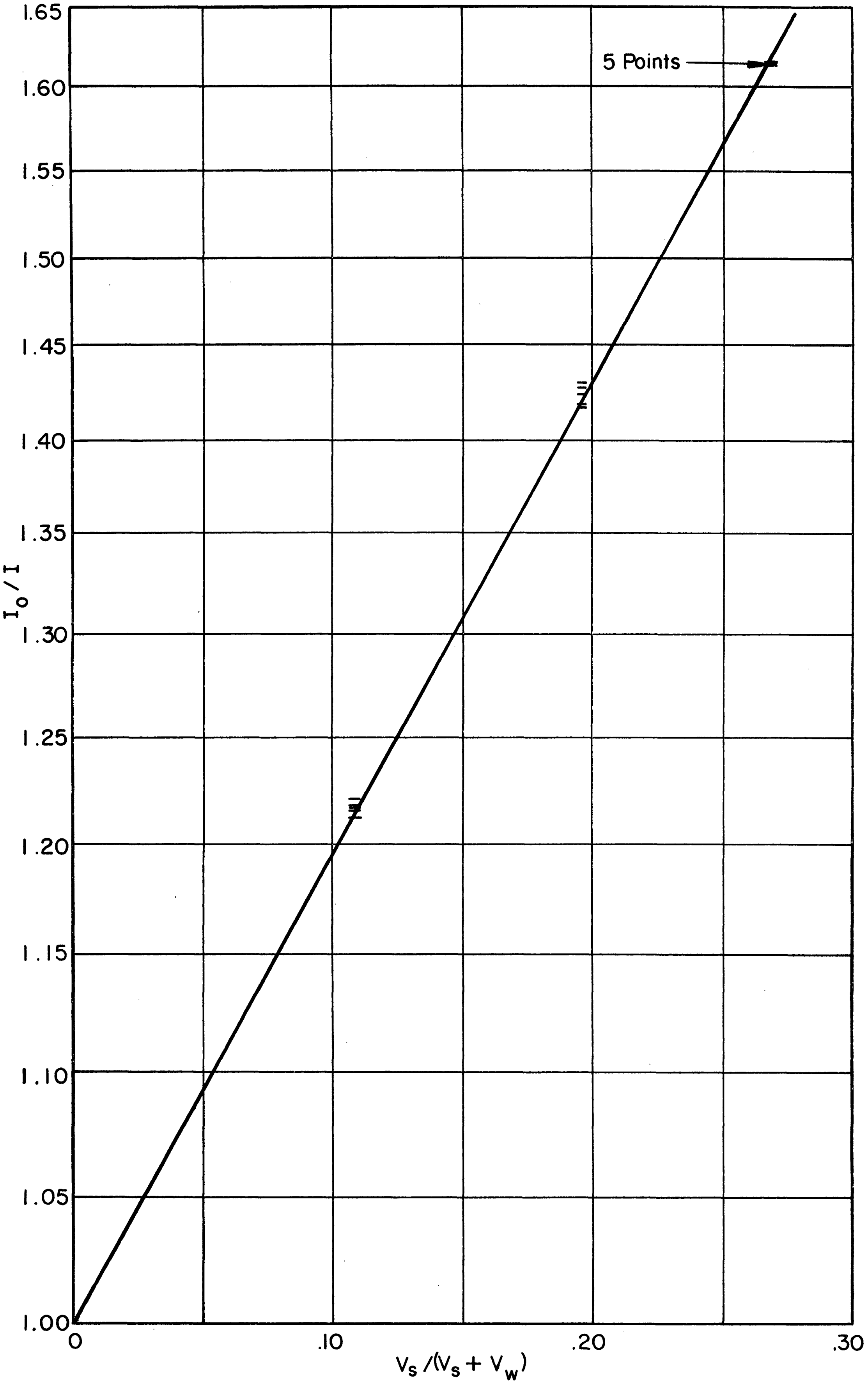

Figure 6. Test data.

TABLE I

Diameter = 0.814 microns V_w = 82 cc.

e	e_M	e_c	e_o/e
Transmission through distilled water. I_o determination, $(I_o)_{ave.}$ = 2.878.			
2.878	2.804	2.878	
2.824	2.743	2.887	
2.808	2.735	2.879	
2.830	2.765	2.870	
10 cc of stock solution added.			
2.319	2.745	2.369	1.215
2.324	2.764	2.358	1.220
2.366	2.807	2.363	1.218
2.331	2.753	2.374	1.212
2.319	2.751	2.364	1.217
10 cc of stock solution added giving total of 20 cc.			
2.015	2.781	2.032	1.416
2.027	2.800	2.030	1.418
1.987	2.767	2.014	1.429
2.029	2.814	2.022	1.423
2.030	2.827	2.013	1.430
10 cc of stock solution added giving total of 30 cc.			
1.779	2.792	1.787	1.611
1.796	2.824	1.783	1.614
1.756	2.783	1.769	1.627
1.787	2.834	1.768	1.628
1.766	2.809	1.763	1.632

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