

A SEDIMENTATION METHOD FOR THE DETERMINATION OF THE PARTICLE SIZE OF FINELY DIVIDED MATERIALS (SUCH AS HYDRATED LIME)

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ABSTRACT

This paper reports a comparison between a sedimentation method of determining particle size distribution and a microscopic method and also some data on hydrated lime. Glass spherules were prepared from pyrex glass and fractionated so that most of the particles had a diameter within 2 microns of the average diameter of the fraction. These particles were then dispersed in a liquid and weighed as they settled out of suspension with an automatic-weighing device. From this sedimentation record the particle size distribution was calculated. The same sample was then used to determine the particle size distribution by measuring the diameters of several hundred particles with a microscope. In making the microscopic measurements the glass spherules were mounted in liquids of various refractive indices and it was found that differences in refractive index of the mounting medium produced appreciable changes in the apparent diameter (more than 20 percent in some cases). The microscopic and sedimentation measurements showed similarly shaped distribution curves but there was some variation between them. Particle size distributions of hydrated lime are also reported.

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I. INTRODUCTION

The fine particles of many finely divided materials are so small that it is impractical to make effective size separations by pneumatic methods and microscopic methods are not readily applicable. Since a knowledge of the particle size of hydrated lime, portland cement, and many other substances may assist in explaining some of their properties, it was considered advisable to attempt to apply a method devised by Oden¹ to determine the particle size distributions of hydrated lime. Oden showed that a mathematical analysis involving Stokes' equation² for the fall of bodies through a viscous medium, will give a

¹ Proc. Roy. Soc. of Edinburgh, vol. 36, pp. 219 to 236, 1915.

² G. G. Stokes, Mathematical and Physical Papers, vol. III, p. 59, Cambridge University Press, 1901. Stokes' original equation was developed for kinematic viscosity.

fineness distribution provided the finely divided material is weighed as it settles out of suspension.

Arnold³ found that individual spheres as small as 130 microns in diameter fall in a viscous medium with a velocity corresponding to that given by Stokes' equation. However, since the particles of many materials such as hydrated lime are very much smaller than the individual spheres used by Arnold, a study was made to ascertain the accuracy with which the particle size distribution could be determined by Oden's method.

Hydrated lime in itself is not a particularly suitable material for this purpose since the particles are irregular in shape and therefore very difficult to measure microscopically. Accordingly the performance of the weighing device was studied with the use of carefully prepared fractions of glass spherules whose diameters could be more readily investigated microscopically. This paper deals therefore with the comparison of the particle size distributions of fractions of glass spherules as ascertained with the sedimentation apparatus, with that determined microscopically. It also contains some data on hydrated lime to show in general the particle size distribution of this material. Just how this factor may be related to other properties of hydrated lime is being investigated.

II. THEORY OF SEDIMENTATION METHOD

In the following discussion, "distribution curve"⁴ means the relation between the percentage of material and the corresponding diameters. A "cumulative curve" shows the amount of material which is coarser than a given size. When a fine material is uniformly dispersed in a liquid and allowed to settle, the curve showing the weight of material settled out as a function of time is a "sedimentation curve."

A distribution curve may be obtained from a sedimentation curve in the following manner.⁵ The amount of material, P , settled on the pan at a given time consists of two parts; one part S , made up of all the particles coarse enough to have settled the entire length of the column, and a second part, consisting of those particles of smaller size which, though they may not have settled the full length of the column, have nevertheless reached the pan. Each size of this second part has a constant settling velocity and the rate of their accumulation on

the pan may be represented as $\frac{dP}{dt}$. At time t , the weight of this

second part, amounts to $t \frac{dP}{dt}$. The total weight, P , settled at time t , is therefore,

$$P = S + t \frac{dP}{dt} \quad (1)$$

³ Phil. Mag., series 6, vol. 22, pp. 755-775, 1911. In "The Electron", University of Chicago Press, 1929, Millikan states that Arnold obtained results which agreed with Stokes' equation for particles having diameters as small as 40 microns.

⁴ F. C. Mills, Statistical Methods. Henry Holt & Co., New York, N.Y., 1924.

⁵ T. Svedberg, Colloid Chemistry, Chemical Catalog Co., 1924.

If for a given time, corresponding to a certain diameter calculated from Stokes' equation, a tangent is drawn to the sedimentation curve, figure 1, the intercept W on the ordinate will be $W = P - t \frac{dP}{dt}$,

but from (1) $S = P - t \frac{dP}{dt}$.

Therefore, $W = S$. Since S is the coarse part of the sediment, the intercept of the tangent divides the sediment into that amount which is coarser than a certain size and an amount finer than that size. The size corresponding to a given time is determined from Stokes' equation:

$$V = \frac{(\rho - \rho')gd^2}{18\eta} \quad (2)$$

in which V is the velocity of a particle falling through a viscous medium, ρ the density of the particle, ρ' the density of the medium g the acceleration of gravity, d the diameter of the particle, and η the coefficient of viscosity of the medium. If W , after being reduced to a percentage basis, is plotted against size, an accumulation curve is obtained from which a distribution curve is derived by plotting the ordinate intercept of equal units of diameter against particle size.

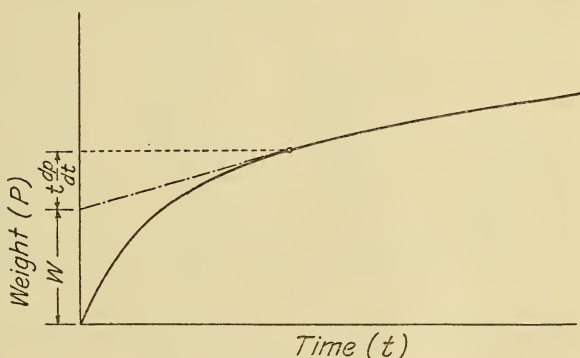


FIGURE 1.—Sedimentation curve.

III. DESCRIPTION AND OPERATION OF SEDIMENTATION APPARATUS

The apparatus with which sedimentation curves were obtained is illustrated in figure 2. The material being analyzed is thoroughly dispersed in a liquid and introduced into the sedimentation cylinder. As the particles settle on the pan attached to the left arm of the balance, the beam is rotated counterclockwise, thus deflecting the image of the lamp from the opaque screen onto a photoelectric cell. This causes an increased current to flow, which, after being amplified by the vacuum tube, operates the relay to start the motor connected with the drum resistance. The motor runs until enough resistance is cut out to increase the solenoid current sufficiently to restore the equilibrium of the balance and throw the light off the photoelectric cell. This is repeated automatically for each effective increment of weight produced by the material settling from suspension. A record of the current flowing through the solenoid circuit then corresponds to a time-weight record of the sedimentation of the sample.

The balance was inclosed in a double-walled cabinet provided with an air circulating system. A heater placed in the circulating system was regulated by means of a grid type toluene regulator in conjunction

with a vacuum tube control similar to the device of D. J. and J. J. Beaver.⁶ The temperature within the balance case, as indicated by a single thermometer, was maintained at 30.0 ± 0.05 C.

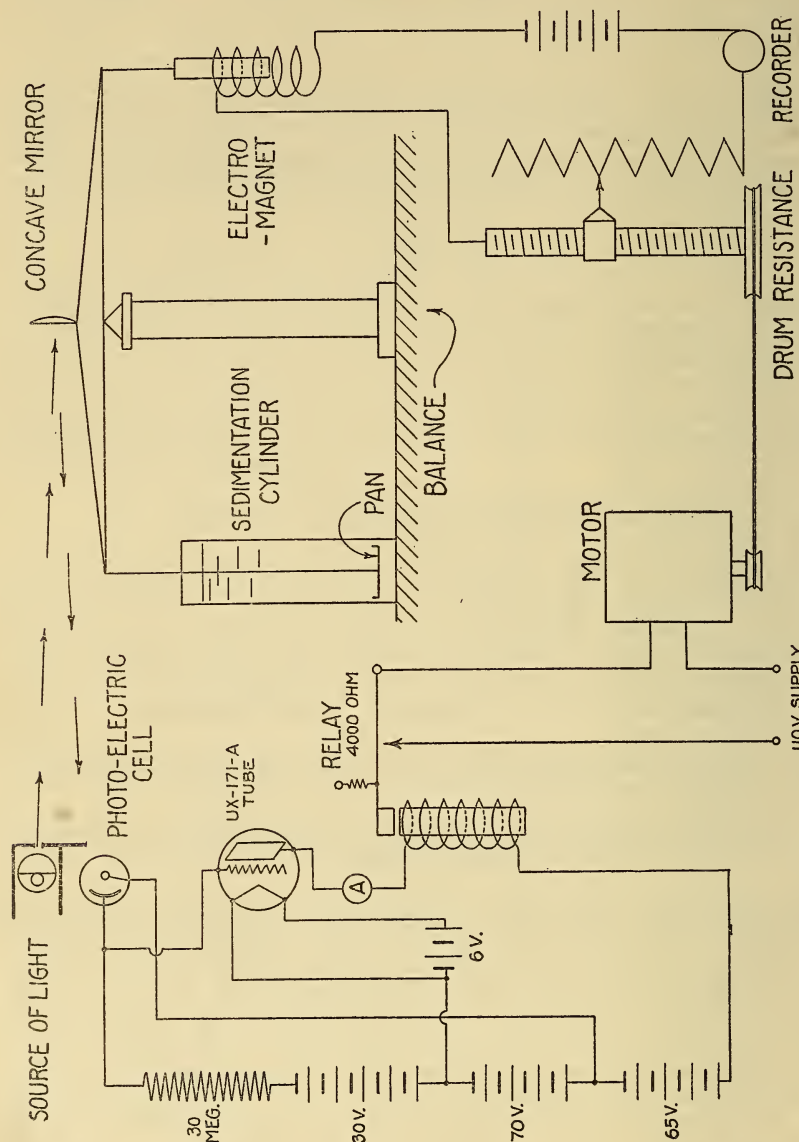


FIGURE 2.—Diagrammatic sketch of automatic weighing apparatus.

In this apparatus the motion of the balance beam is restricted by the stirrup arrests, and reliable operation was not obtained until agate bearing stirrup arrests were used.

A concave mirror having a focal length of 35 cm and a diameter of 8 cm was attached to the balance beam at its axis of rotation. The magnet attached to the right end of the beam was of cobalt-magnet steel which was annealed before being magnetized.

⁶ Jour. Ind. Eng. Chem., vol. 15, pp. 359-361, 1923.

In order to measure the current in the solenoid circuit, a recording potentiometer was used to measure the drop in voltage at the potential terminals of a suitable shunt. The potentiometer was a double range instrument and the shunt so chosen as to use nearly its entire range. A 50-cm scale was thus available on which to record the current. The entire scale was calibrated by adding weights to a supplemental balance pan above the liquid and between the balance beam and the sedimentation pan. The system was found to be accurate to about 0.2 mg.

The drum resistance in series with the solenoid was made by winding no. 20 advance wire in a groove on a hard-rubber drum. A transparent celluloid cover was provided for the drum resistance to protect it from dust, but it was necessary to clean the wire occasionally with vaseline.

To obtain a sedimentation curve, the material to be analyzed was placed in the sedimentation cylinder and butyl alcohol added to bring the level of the suspension nearly to a prescribed level. The suspension was then agitated for 30 minutes with a mechanical stirring device in order to disperse the material. The temperature of the suspension was next adjusted to the temperature of the cabinet, the sedimentation pan inserted, and the level of the suspension adjusted by adding butyl alcohol until the liquid just touched a wire suspended a definite distance below the top surface of the cylinder. (The depth of the liquid to the pan was either 21.7 or 10.85 cm). Meanwhile segregation was prevented by moving the pan up and down. The cylinder was then placed in the balance case, the pan attached to the beam and the automatic weighing device started immediately.

In the reduction of the sedimentation data, the tangents to the sedimentation curves were calculated by the method of least squares as developed by F. T. Gucker and H. J. Brennen.⁷

IV. PREPARATION AND MICROSCOPIC MEASUREMENTS OF GLASS SPHERULES

In order to make a comparison between the microscopic and sedimentation methods it was desirable to have a material whose dimensions could be measured microscopically with considerable accuracy. Such a material was made by grinding pyrex glass in a steel ball mill. Most of the adventitious iron was then removed with a magnetic separator and the remainder by treatment with dilute hydrochloric acid and distilled water. The powdered glass was then dried and introduced into the air line of a blast lamp.⁸ The glass fused while passing through the flame and assumed a spherical shape, as is shown by the photomicrographs (fig. 3). Repeated fractional sedimentations in ethyl alcohol were made and finally four fractions, each of which had a small range of sizes, were obtained. A portion of each of these four fractions was weighed and combined to make a composite sample.

In order to obtain distribution curves for comparison with the sedimentation method, the particle size of each fraction was determined microscopically. For this purpose a microprojector was used

⁷ Jour. Am. Chem. Soc., vol. 54, pp. 886-888, 1932.

⁸ The author is indebted to F. G. Cottrell and C. G. Gilbert for this method of preparing the glass spherules.

in which the light from an arc lamp, after passing through a water cell and an abbé condenser, was sent through a microscope and projected onto a screen. The magnification, obtained with a 4 mm objective, was about 2,600 diameters and with a 1.9 mm immersion objective, about 5,700 diameters, determined by projecting a 100 micron interval of a calibrated stage micrometer on a screen. The projected field was examined with 10-micron intervals and only the undistorted portion of the field was used when measuring the diameters of the spherules.

The effects of changes in adjustments of the microscope were investigated by measurements on a number of particles. If the focus on a particle was changed so that the Becke⁹ line appeared either outside or inside the particle, no change in diameter could be detected. Changing the diaphragm opening and lowering the abbé condenser several millimeters had no appreciable effect on the observed diameter. Although these changes produced no measurable effects, all measurements were made under similar conditions, the microscope always being focused so that the Becke line just disappeared.

The particle size distribution of each fraction was determined on the material removed from the sedimentation apparatus. For this purpose the fraction was thoroughly dispersed in the butyl alcohol and a small quantity placed on a microscope slide. A cover glass was put on and worked over the suspension until nearly all the alcohol had evaporated. The cover glass was then removed and the residual alcohol evaporated. A mounting medium of known refractive index was then put on the slide and the cover glass worked around until an evenly dispersed layer of particles was obtained. Under the microscope these particles appeared well defined, making it possible to accurately measure their apparent size. The diameter of each particle was measured to one-quarter micron and the particles were classified in half-micron intervals. When the mean diameters of different groups of about 100 particles each were calculated, good agreement was obtained provided the particles were always mounted in the same mounting medium. For example, the mean of six such groups (measured from three slides by three observers) was 6.07 microns with a standard deviation of 0.09 micron. Although this agreement held when changes in mounting media were made, the apparent diameter changed with change in mounting medium, as is shown in figure 4 where the arithmetic mean particle size is plotted against refractive index of the mounting medium. Measurements were not made in mounting oils having indices between 1.52 and 1.42 because of the low relief in such oils. (The refractive index of the glass was 1.47.) Since each point represents the arithmetic mean diameter of from 200 to 400 particles and the same order of change occurs in all three fractions, it is hard to account for these differences as observational errors.

Measurements were also made on individual spherules by means of a filar micrometer. A permanent mounting of glass spherules was obtained by heating a microscope slide, to such a temperature that the spherules fused to the slide and yet did not become imbedded to any appreciable extent. Scratches on the slide, made with a glass cutter, aided in finding a given field. Individual particles in a field

⁹ A. N. Winchell, *Elements of Optical Mineralogy*, part I, p. 70, John Wiley & Sons, 1928.

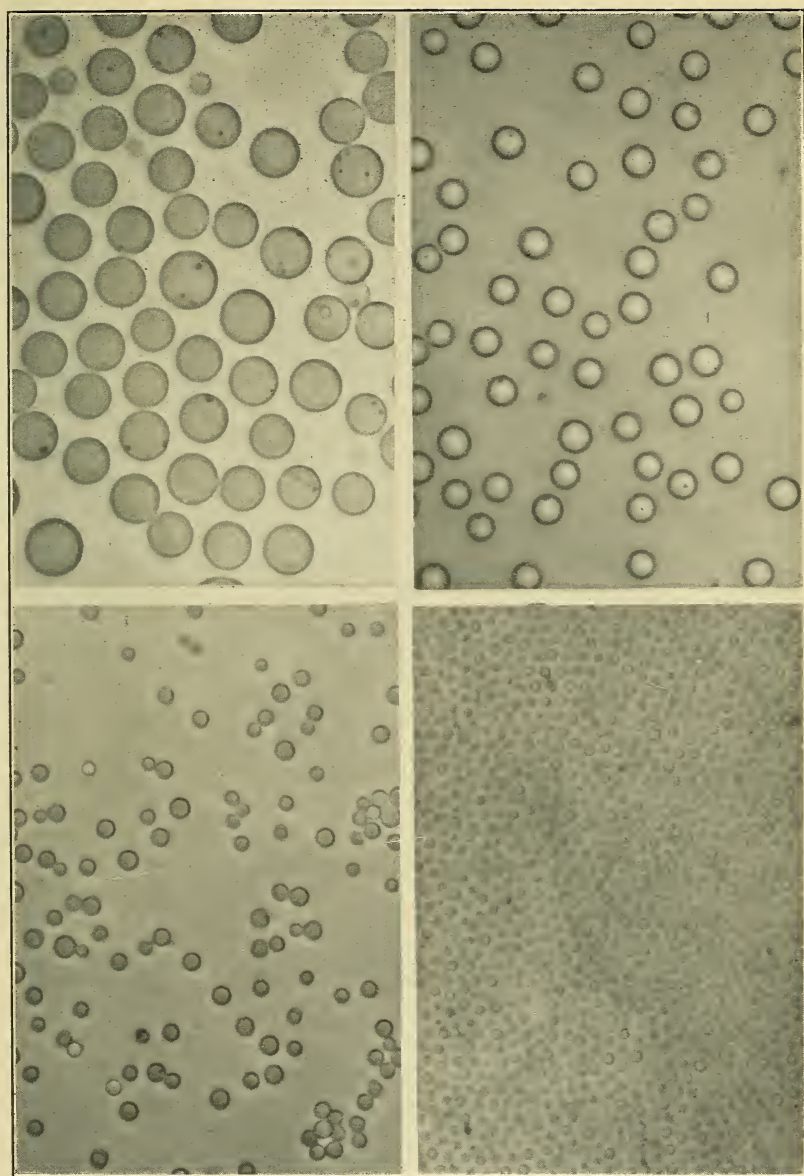


FIGURE 3.—Photomicrographs of the four fractions of glass spherules.
(All magnified 700 diameters.)

could be identified and measurements were made on these particles when immersed in mounting media of various refractive indices. These measurements are also shown in figure 4. The standard deviation of each of these points is considerably less than 0.1 micron. The order of variation is the same as was found on the fractions of glass spherules. Measurements made with and without critical illumination did not change the results.

It appears, therefore, that in making measurements of particle size with a microscope, there must be taken into account the effect

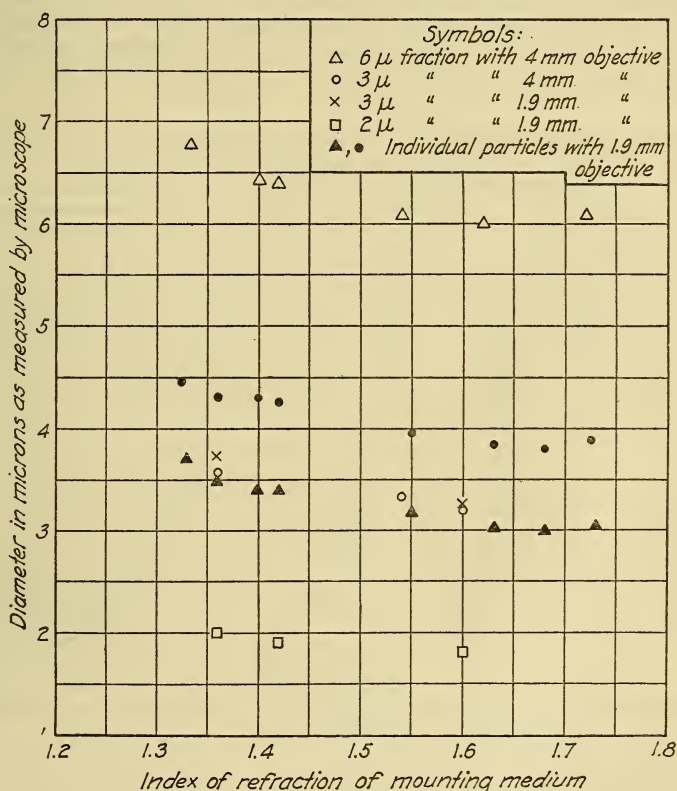


FIGURE 4.—Effect of change in index of refraction of mounting medium on microscopic measurements of diameters of glass spherules ($N_d=1.47$).

produced by the mounting medium. Although this phenomenon has been reported in the literature,¹⁰ many investigators have not considered its effect when measuring particle size. No other method was used to determine the true particle size distribution of the fractions and this paper, therefore, reports only a comparison between the microscopic and sedimentation methods. The microscopic distributions chosen are an average of measurements made in mounting media whose indices were approximately 1.40 and 1.60. These values were arbitrarily chosen but it is not known whether or not this gives true particle size.

¹⁰ For instance W. Marshall mentions this change of size in "The Influence of Refractive Index on Mounting Media", Jour. Roy. Mic. Soc., vol. 52, pp. 275-280, 1932.

V. DISPERSION OF GLASS SPHERULES FOR SEDIMENTATION

The accuracy of any sedimentation method will depend largely upon having the sample of the particulate material completely dispersed. Two sources of difficulty were experienced in dispersing these fractions of glass spherules. It was found that whenever a dispersion medium was allowed to evaporate from the glass spherules they caked together and dispersed again only with difficulty. Apparently a minute quantity of material, left on the surface, bound the particles together and even the same liquid from which they were evaporated would not redisperse them. However, when these spherules were treated with a mixture of hot chromic and sulfuric

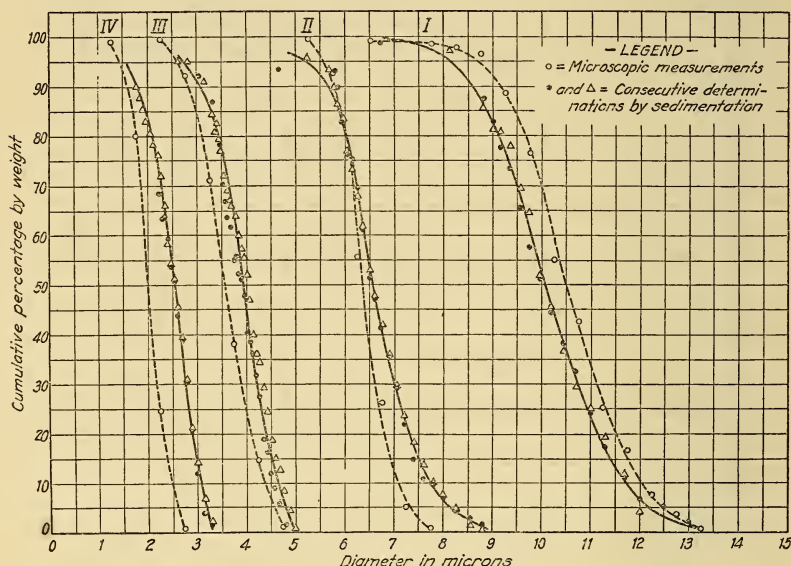


FIGURE 5.—Distribution of sizes of four fractions of glass spherules as determined by microscopic and sedimentation measurements.

acids, followed by washing with water, ethyl alcohol and butyl alcohol, better dispersion was obtained. Another source of difficulty occurred after the spherules had been kept in butyl alcohol for a long time. In weighing portions of the four fractions to make the composite sample, it was noticed that a film of organic material remained on the glass spherules after evaporation of the butyl alcohol. This film was readily removed by treatment with a mixture of hot chromic and sulfuric acids. Better dispersion was obtained after treatment with these acids than before the treatment, as was indicated by better agreement of the mean values and standard deviations with the corresponding measures of the microscopic data. All the sedimentation results reported in this paper were obtained on fractions which had been given this acid treatment.

VI. COMPARISON OF MICROSCOPIC AND SEDIMENTATION MEASUREMENTS

The results of the microscopic and sedimentation measurements are given in figures 5 and 6 in which cumulative percentages are plotted against particle size. The data of figure 5 and the calculated surface values are also summarized in table 1. The reduction of the sedimentation data gives a distribution by weight and the microscopic measurements were, therefore, calculated to a weight basis.¹¹ The cumulative curves of the sedimentation data were obtained by the method previously outlined by using the following numerical values in equation (2):

$$\rho = 2.21,^{12} \quad \rho' = 0.804, \quad \eta = 0.0231 \quad \text{and} \quad g = 980 \quad (\text{cgs units})$$

TABLE 1.—Comparison of microscopic and sedimentation determinations of the particle size of four fractions of glass spherules

Fraction no.	Weight distribution				Surface distribution			
	Mean diameter		Standard deviation		Mean diameter		Surface per gram	
	Microscopic	Sedimentation	Microscopic	Sedimentation	Microscopic	Sedimentation	Microscopic	Sedimentation
	$\frac{\sum nd^4}{\sum nd^3}$	$\frac{\sum n'd}{\sum n'}$	$\sqrt{\frac{\sum nv^2}{\sum n}}$	$\sqrt{\frac{\sum n'v'^2}{\sum n'}}$	$\frac{\sum nd^3}{\sum nd^2}$	$\frac{n'}{\sum \frac{d}{n'}d}$	$\frac{6 \times 10^4}{\rho d'}$	$\frac{6 \times 10^4}{\rho d'}$
I.....	μ 10.7	μ 10.1	μ 1.27	μ 1.21	μ 10.5	μ 9.9	cm^2/g 2,590	cm^2/g 2,730
II.....	6.5	6.6	.50	.86	6.4	6.5	4,240	4,160
III.....	3.7	3.9	.54	.59	3.6	3.8	7,600	7,200
IV.....	2.1	2.5	.41	.45	2.0	2.4	13,400	11,300

d = midpoint of class.

n, n' = class frequency.

σ = deviation from mean.

d' = surface mean diameter.

These cumulative curves (figs. 5 and 6) show a similarity of shape for the two methods. For all fractions this similarity holds, not only for the general shape of the curves but also for the range of sizes. The mean value of the 10-micron fraction, as determined by sedimentation, is smaller than the microscopic determination, while for the three smaller fractions the sedimentation values are greater than the microscopic values. These deviations produce a difference of about 6 percent on the calculated surface of the 10-micron fraction, 2 percent on the 6.5-micron fraction, 5 percent on the 3.5 and on the 2-micron fraction 16 percent.

Since it was not determined which refractive index of mounting medium will give true particle size when glass spherules are measured with a microscope, no attempt has been made to explain the differences found or to obtain better agreement between sedimentation and microscopic data.

Coutts and Crowther,¹³ and Shaw and Winterer¹⁴ reported that, under certain conditions, the percentage of material settling on a

¹¹ Perrot and Kinney, Jour. Am. Ceram. Soc., vol. 6, pp. 417-439, 1923.

¹² The density of the powdered glass from which the spherules were made was 2.25.

¹³ Trans. Farad. Soc., vol. 21, pp. 374-380, 1925.

¹⁴ Int. Cong. of Soil Science, vol. 1, pp. 384-393, 1927.

pan suspended in a disperse system is not proportional to the relative area of the pan and the cross-sectional area of the container. In the current investigation some of the 6-micron fraction (which had been kept in ethyl alcohol) was dried, weighed, and redispersed in the sedimentation cylinder. At the end of 48 hours 167 mg had settled on the pan, whereas the calculations indicated that 168 mg should have been recorded. After a sedimentation of the 10-micron fraction, the material settled on the pan and also that which settled on the bottom of the cylinder were carefully removed and their particle sizes determined microscopically. The arithmetic mean diameter of 900 particles of the material collected on the pan, was 9.84 microns, and the corresponding value of 869 particles from the bottom of the cylinder, was 9.81 microns. Since this difference is of no significance it is believed that the material settling on the pan was representative of all the material placed in the sedimentation cylinder.

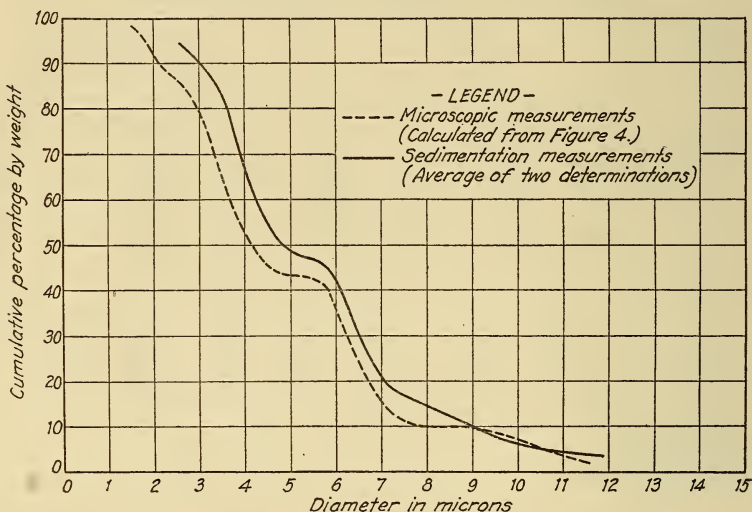


FIGURE 6.—Distribution of sizes of a composite sample containing portions of the four fractions shown in figure 3.

VII. PARTICLE SIZE OF HYDRATED LIME

Although it has not been demonstrated that the sedimentation apparatus gives true particle size, the error involved is probably not too great for an initial study of the relation between particle size and other properties of lime. Sufficient limes have not been studied so far to be able to correlate particle size with other properties but there is included a table showing the particle size of a few limes in order to show the range of sizes encountered in commercial hydrated limes. The indicated diameters in the table were calculated from Stokes' equation and are therefore the diameters of spheres having the same settling velocity and density (2.3 for high calcium hydrates and 2.5 for dolomitic hydrates) as the lime particles.

TABLE 2.—Particle sizes of nine hydrated limes

Diameters	Percentages coarser than given size								
	High calcium hydrates, sample numbers					Dolomitic hydrates, sample numbers			
	1	2	3	4	5	6	7	8	9
μ	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
40.....	6	1	5	2	2	6	15	8	12
30.....	9	1	6	3	3	9	20	11	17
20.....	13	2	9	8	6	13	27	20	22
10.....	25	10	20	30	27	35	40	35	38
5.....	70	55	55	80	68	81	65	58	62
3.....	90	80	81	94	92	-----	-----	85	86

VIII. CONCLUSIONS

Microscopic measurements on glass spherules have shown that changes in refractive index of the medium surrounding the particle alter the apparent diameter of the particle. The magnitude of this change is such that until it is known which refractive index will give true particle size, the microscope certainly has limited use as a means of determining particle size. When fractions of these glass spherules were well dispersed in butyl alcohol, fair correlation of particle size distribution was obtained between sedimentation measurements and an average of microscopic measurements. Since this correlation was obtained, the sedimentation method was considered sufficiently accurate to make particle size measurements of hydrated lime.

WASHINGTON, October 28, 1933.