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PARTICLE SIZES OF CLAY MINERALS BY SMALL-ANGLE *X*-RAY SCATTERING[1]

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ABSTRACT

This paper describes an investigation of small-angle *x*-ray scattering as a possible technique for determining the particle size of clay minerals. The method used is that of Shull and Roess (1947) involving a graphical comparison of experimental scattering curves with theoretical curves. In theory, both the distribution of particle sizes and the shape of the particles should be obtainable, but in this study the particle shape was assumed. Descriptions of the method and of the two-crystal spectrometer used to collect the scattering data are included as well as data obtained for nineteen clay samples.

INTRODUCTION

The common characteristic of all clay minerals is their small particle size. Essentially, it is this small size, often given as below two microns, which distinguishes them as a group and is responsible for many of their properties. Because of its importance, a number of methods have been developed for measuring the size of clay particles, such as settling rates, electron microscopy, light scattering, surface area measurements, and *x*-ray diffraction line broadening. All of these have their limitations and there is still a need for a good general method of measurement. Another technique, small-angle *x*-ray scattering, has been used to measure the size of particles in the region below 1,000 Å. Its applicability to larger particles is in doubt, but West (1952) used it in studying clay suspensions in water, and Norrish and Rausell-Colom (1963) examined the swelling of montmorillonite and vermiculite by this method.

The paper reports on some of the results obtained in a study of the small-angle *x*-ray scattering from clay minerals, completed in 1954. Since then, comparatively little information on this subject has been published and this somewhat dated material is submitted in the hope that it will be of use in clay research.

THEORY

It is known that finely divided materials scatter intensity from an *x*-ray beam in the same way that small opaque particles scatter light from a luminous beam. The intensity of this scattered radiation diminishes with increasing angular divergence from the unscattered beam and the rate of this decrease with angle is dependent on the size of the scattering particles, their shape, and their state of aggregation. Numer-

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[1] Extracted from an unpublished Ph.D. dissertation, University of Columbia, 1954.

[2] Operated with support from the U. S. Air Force.

ous papers have been published on the theory, experimental technique, and results of small-angle *x*-ray scattering research. General treatments of the theory are given by Guinier (1955) and Yudowitch (1953), and a bibliography of the literature on small-angle *x*-ray scattering and associated topics up to 1952 has been compiled by Yudowitch (1952).

If we assume particles with a uniform size which scatter independently, and have a shape which can be expressed as a spheroid with principal axes R, R and vR, then, neglecting refraction effects, the general equation for the intensity scattered at an angle ϵ from an *x*-ray beam can be shown to be:

$$I_\epsilon = I_e C^2 \left(\frac{\sin u - u \cos u}{u^3}\right)^2$$

where $u = R\xi\ (\sin^2\theta + v^2\cos^2\theta)^{1/2}$, $2\theta = \epsilon$, $\xi = 4\pi \sin\theta/\lambda$, I_e = the intensity scattered by a single electron, and $C = \frac{4}{3}\pi R^3 \rho$, where ρ is the electron density of the particles. Various methods based on this equation have been used to obtain particle sizes from small-angle *x*-ray scattering. Because clay minerals possess a strong shape factor as well as a wide range of sizes, a method of small-angle scattering analysis developed by Shull and Roess (1947) was selected for this study.

This method involves the use of the above equation, further incorporating in it a size distribution function—Maxwellian, Gaussian or rectangular. From the resulting equation a theoretical scattered intensity curve is calculated for each of several particle shapes and size distributions. The calculations are involved, and only those theoretical curves which were already derived by Shull and Roess were used in this study. A complete description of the derivation of the standard curves and their use is presented in two papers by Shull and Roess (1947) and Roess and Shull (1947). No size distribution can be obtained by this method other than in the form of the particular distribution function used in calculating the theoretical curves. It was felt that the Maxwellian distribution would be a good approximation to natural samples.

The Maxwellian distribution function which was used is:

$$M(R) = B\left(\frac{R}{R_0}\right)^n \exp. - \left(\frac{R}{R_0}\right)^2$$

where

$$B = \frac{2}{R_0 \Gamma \dfrac{(n+1)}{2}}$$

R_0 and n are factors which determine the size distribution, M(R) is the mass of sample having radius R, and B is a factor included to give the total mass a value of unity. The nature of this function is shown by Fig. 1 in which distribution curves are plotted for n equal to 1, 2, 3 and 5, with R_{max} (the peak of the distribution curve) at 1000 Angstroms. R_{max} can be calculated from the equation:

$$R_{max} = (n/2)^{\frac{1}{2}R_0}$$

As shown by the figure, R_0 is not a direct indication of the particle radius, but from it and n a particle size distribution can be derived. The area under all of the curves is the same, but with increasing n the distribution curves become narrower.

The theoretical scattering curves are plotted as log $K^{-1}I(\xi, v)$ versus log $R_0^2\xi^2$, where K^{-1} is a factor included to give the intensity a value of one when $R_0^2\xi^2=0$. Sets of theoretical curves for $v=10$, 1, 0.25 and 0 and $n=0$ to 5 were available. Figure 2[1] shows the set of curves for $v=0$ which was found most useful in analyzing clay mineral scattering. The theoretical curves can be seen to possess three distinct features: (a) a flat section at very small angles, (b) a curved region, the knee of the curve, at intermediate angles, and (c) a steep, linear section at larger angles. It is the knee of the curve which permits the matching of the experimental with the theoretical curves and no information can be extracted if the experimental curve does not show it.

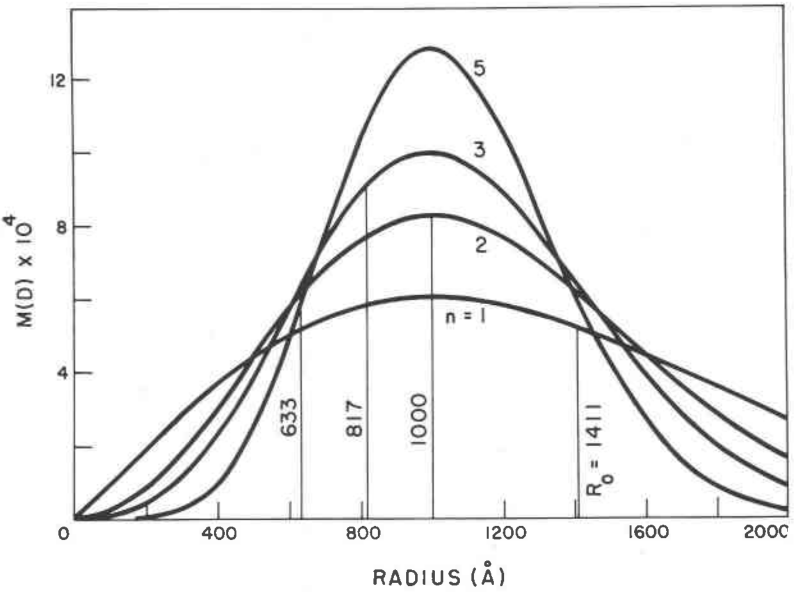

FIG. 1. Maxwellian distribution curves with $n=1, 2, 3$ and 5, calculated for $R_{max}=1000$ A.

The experimental data are plotted as log I versus log ξ^2, and on

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[1] Redrawn from the *Journal of Applied Physics* **18** (1947).

matching an experimental curve to one of the theoretical curves a value of R_0 can be obtained by a comparison of the abscissae. The particular theoretical curve for which the match is obtained gives both v, the particle shape factor, and n, the size distribution factor. The factor v gives an approximation of the shape of the particles in the form of spheroids with axes R, R and vR. For $v=1$ they are spheres, for v less than one they are oblate spheroids, and for $v=0$ they are very thin disks. For flake-like particles the best approximation of the shape is given by $v=0$, but in this case nothing can be said about the thickness except that it is small compared to the diameter. The use of a small value such as $v=0.1$ instead of $v=0$ will make very little difference in the theoretical scattering curves.

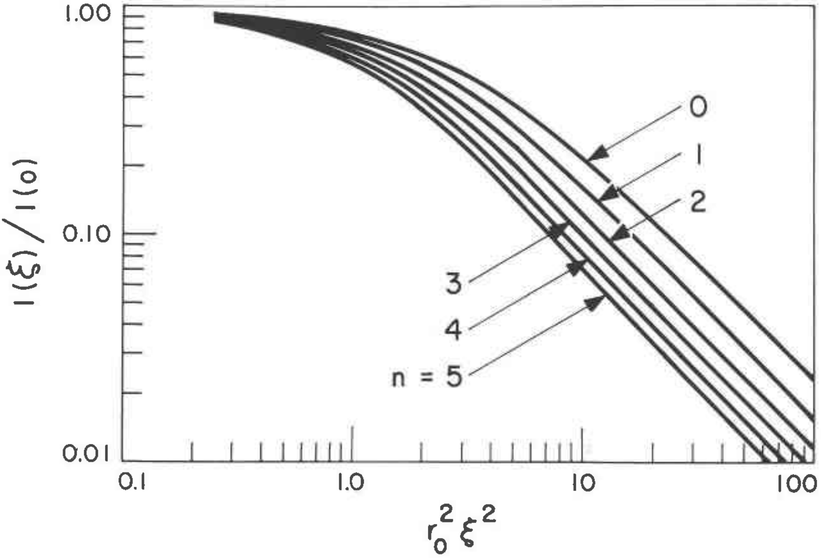

FIG. 2. Calculated scattering curves for Maxwellian distributions of thin disks, $v=0$.

By substituting R_0 and n in the equation for the Maxwellian function given above, a mass distribution curve can be derived for the sample. The average particle radius $\overline{R}$ is obtained from the following table taken from Shull and Roess (1947):

n =	0	1	2	3	4	5
$(\overline{R}/R_0)^2$ =	0.227	0.693	1.183	1.677	2.176	2.674

and from this we can get the average particle diameter $\overline{D}$, the particle size which divides the mass distribution in half. R_{max} is calculated from the equation:

$$R_{max} = (n/2)^{\frac{1}{2}R_0}$$

and from this we obtain D_{max} which is the particle size at the peak of the mass distribution curve.

INSTRUMENTATION

A number of different methods have been used in the study of low-angle scattering of *x*-rays. The most interesting region is within one degree of the direct beam and the accurate measurement of intensities in this region, without interference by the direct beam, requires special techniques. For this research, a two-crystal spectrometer, designed by Dr. L. A. Siegel and the writer, was used. A diagram of its construction is given in Fig. 3. As it was designed to be as inexpensive as possible consistent with the required accuracy, many convenient adjustments were omitted.

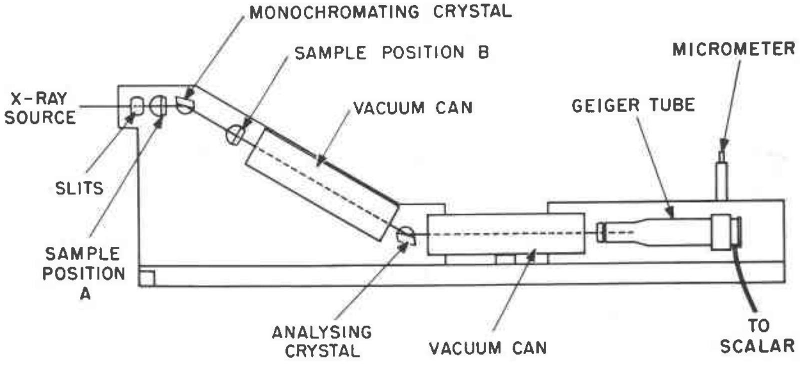

FIG. 3. Diagram of the construction of the two-crystal spectrometer showing the path of the *x*-ray from source to Geiger tube.

Essentially this instrument consists of a stationary crystal to monochromate the *x*-ray beam, a movable crystal to analyze the scattered radiation, a micrometer to rotate the crystal through very small angles, and a Geiger tube to measure the radiation from the second crystal. For the crystals, two cleaved rhombs of Iceland spar were used. The freshly cleaved surfaces were lightly ground and polished and then etched with dilute acid. The half-height breadth of their rocking curve was 11″. The first crystal is adjusted to the reflecting position for the characteristic *x*-radiation used (in this case CuKα). Since a parallel beam is desired, slits are placed in front of this crystal to reduce the divergence of the *x*-ray beam due to the finite size of the *x*-ray source. Two sample positions are used: A, before the first crystal, and B, after the first crystal. The second crystal, the analyzer, is rotated by means of a 40 centimeter arm which is driven by a micrometer. The micrometer is graduated in divisions of 0.01 millimeter, so that an adjustment of one division on the micrometer moves the analyzing crystal through approximately 5″ of arc. In order to cut down on air scattering, two vacuum cans are used, one between the sample and the second crystal, and the other between the second crystal and the Geiger tube.

The operation of this spectrometer is simple. A parallel beam of monochromatic *x*-rays is obtained from the first crystal. With the sample at position B, some of the intensity is scattered out of this beam. When the second crystal is in a position parallel to the first crystal, it diffracts the direct beam into the Geiger counter, but when it is rotated away from this position it diffracts the radiation scattered at that angle into the Geiger tube. Thus we can measure the intensity of the radiation scattered at various angles from the direct beam.

The direct beam, however, is not strictly confined to a single direction. It has a definite width and contributes to the measured intensity at a considerable angle to its peak position. A correction for this direct beam contribution must be applied to the measured scattering curve. This is done by placing the sample in position A and duplicating the readings taken with the sample in position B. When the sample is in position A, the scattered radiation is not reflected by the first crystal, and only the direct beam component is measured at each position of the second crystal. Subtracting the readings for position A from those for position B gives a scattering curve corrected for the direct beam. This method also corrects for the Geiger tube background.

The *x*-ray source was a Phillips unit with stabilized current and voltage and a Cu-target tube operated at 40 kV and 18 ma. The intensity of the primary beam was monitored and the *x*-ray intensities were corrected for non-linearity of the Geiger tube. The sample holder consisted of a piece of sheet metal with a $\frac{1}{4}''$ hole. Several of these of different thicknesses were made and the best sample thickness was determined by measuring the scattered radiation at a point about 1′ from the direct beam for each of the holders. Most of the clays were run with sample thicknesses from .2mm to .5mm. The samples were ground to a fine powder and pressed into the holder just tightly enough to stand handling.

The experimental procedure was as follows: the sample was placed in position B and readings were taken at about $2\frac{1}{2}''$ intervals, starting a little before the center of the beam. By reading over the beam, its position

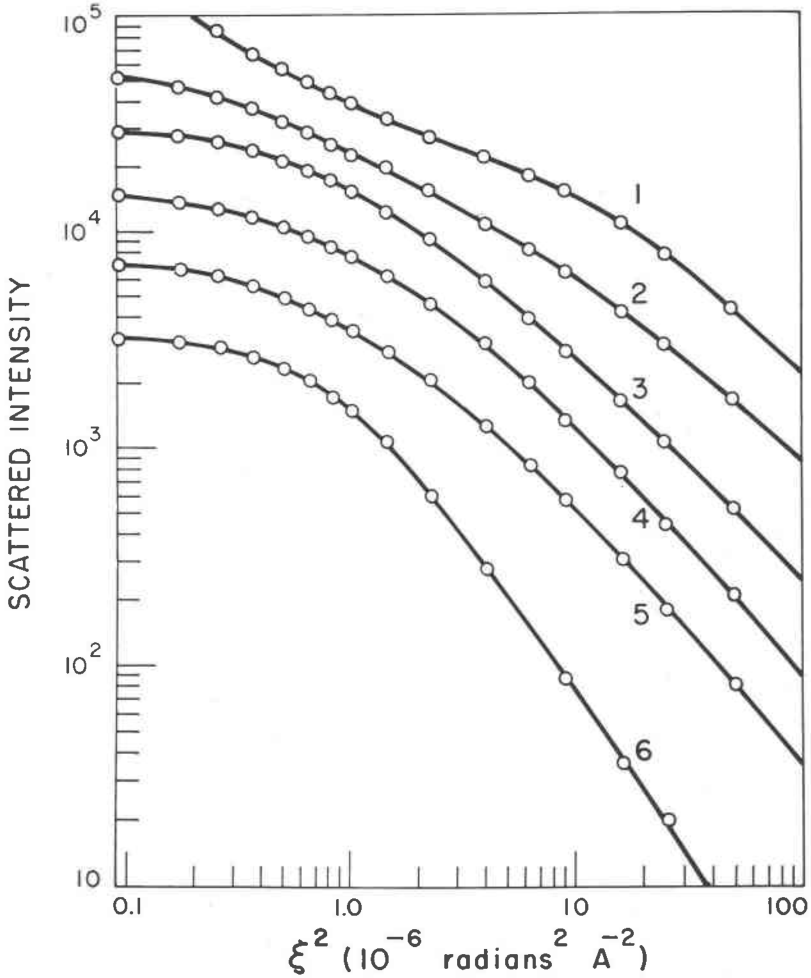

FIG. 4. Experimental scattering curves for kaolinites.

could be determined with an accuracy of about 1″. Once the position of the center of the beam was determined, readings were taken at gradually increasing intervals until the interesting region was covered. The same procedure was then followed with the sample in position A. The determination of the position of the beam each time was necessary because of the thermal expansion of the micrometer shaft. The amount of expansion which occurred while the instrument was in operation for six hours was sufficient to change the position of the center of the direct beam with respect to the micrometer readings by about 5–10″. Measurements taken at less than 15″ from the direct beam were found to be erratic and the region below this was not used.

PARTICLE SIZE OF CLAY MINERALS

The clay minerals examined in this study are kaolinites, montmorillonites and illites. It was hoped that attapulgites and halloysites could be treated using theoretical curves with a shape factor $v = 10$ but these had a very shallow knee and no reasonable match could be obtained for

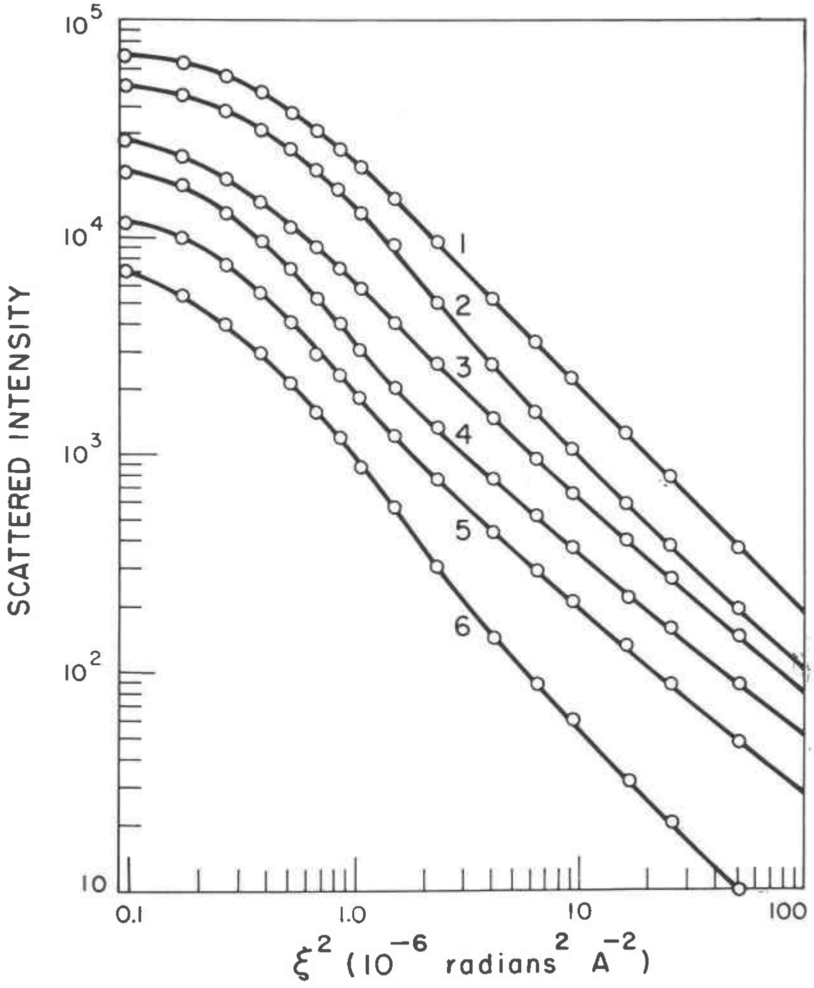

FIG. 5. Experimental scattering curves for montmorillonites.

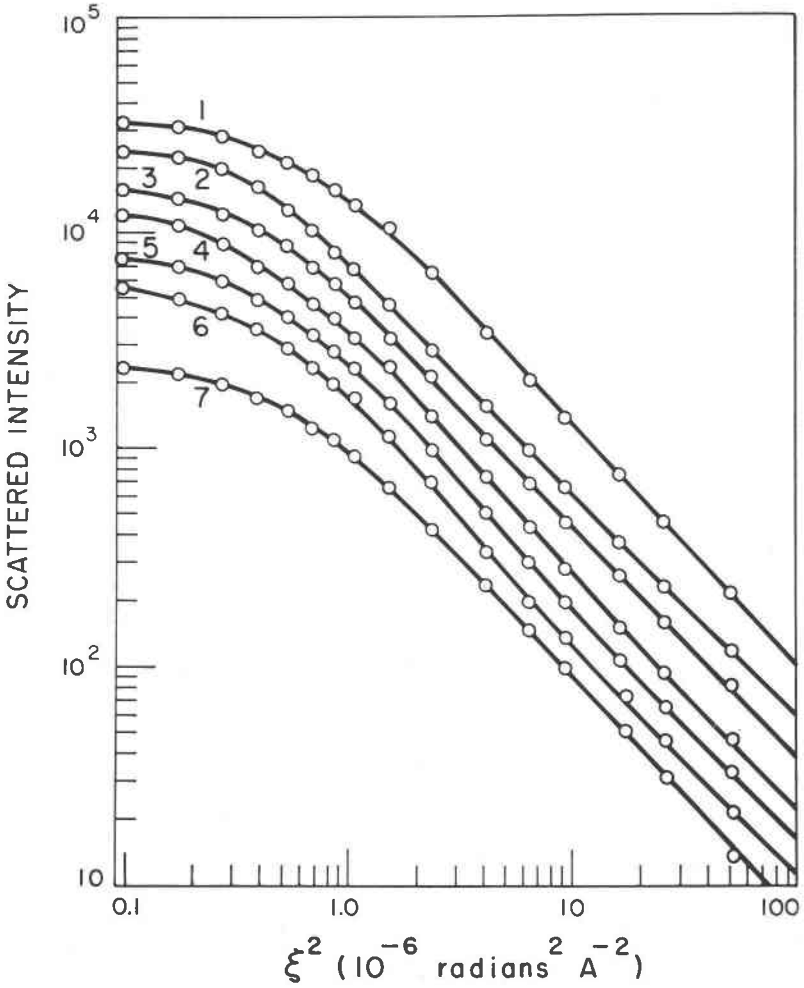

FIG. 6. Experimental scattering curves for illites and interlayered illite-montmorillonites.

the experimental curves. Sixteen samples were selected from the reference clay mineral specimens of Project 49, American Petroleum Institute, see Kerr *et al.* (1950b). To these a poorly crystallized kaolinite from Sayreville, New Jersey, a lathlike illite from Gilman, Colorado, and a hydrothermal illite from Marysvale, Utah were added. The small-angle *x*-ray scattering curves obtained as described under Instrumentation are shown in Figs. 4, 5 and 6. The samples and their scattering curves are identified in Table 1.

It was hoped that both the shape and the size distribution of the clay particles could be determined, but the only good fits of the experimental curves to theoretical curves were with those having $v=0$. Therefore it was decided that a particle shape factor $v=0$ would be assumed and this set of theoretical curves, shown in Fig. 2, was used throughout. As a result nothing can be said about the thickness of the clay particles other than that it is small compared to the diameter.

TABLE 1. LIST OF CLAY SAMPLES EXAMINED

Sample	Locality	API#49 No.	Figure No.
Kaolinite	Murfreesboro, Arkansas	1a	4-1
Kaolinite	Bath, South Carolina	5	4-2
Kaolinite	Macon, Georgia	3	4-3
Kaolinite	Mesa Alta, New Mexico	9a	4-4
Kaolinite	Sayresville, New Jersey		4-5
Dickite	San Juanito, Chihuahua, Mexico	15c	4-6
Montmorillonite	Clay Spur, Wyoming	26	5-1
Montmorillonite	Chambers, Arizona	23	5-2
Montmorillonite	Santa Rita, New Mexico	11	5-3
Montmorillonite	Burns, Mississippi	21	5-4
Montmorillonite	Otay, California	24	5-5
Montmorillonite	Lorena, Mississippi	20	5-6
Illite	Fithian, Illinois	35a	6-1
Illite	Morris, Illinois	36	6-2
Illite	Marysvale, Utah		6-3
Illite	Gilman, Colorado		6-4
Illite-Montmorillonite	Highbridge, Kentucky	42	6-5
Illite-Montmorillonite	Pioche, Nevada	32	6-6
Illite-Montmorillonite	Cameron, Arizona	31	6-7

The results obtained for nineteen clay samples are given in Table 2. Only R_0, n, $\overline{D}$ and D_{max} are given, but from R_0 and n a mass distribution can be derived. As a measure of the reliability of the results, an estimation of the degree of fit of the experimental curves with the theoretical curves is included using the following terms:

1. Very good: a fit within experimental error over the whole curve.
2. Good: a close fit over most of the curve.
3. Fair: a close fit at the knee but a deviation at large angles, probably due to the size distribution lying between two of the theoretical curves.
4. Poor: a fit only at the knee.
5. None: no match obtained.

TABLE 2. SMALL-ANGLE SCATTERING DATA FOR CLAY SAMPLES

Sample	API#49 No.	Figure No.	Degree of fit	n	R_0	D_{max}	$\overline{D}$
Kaolinite	1a	4-1	Poor	1	450	640	750
Kaolinite	5	4-2	None				
Kaolinite	3	4-3	Fair	1	1590	2300	2700
Kaolinite	9a	4-4	Fair	1	1670	2400	2800
Kaolinite		4-5	Fair	1	1900	2700	3200
Dickite	15c	4-6	Poor	5	1310	4200	4300
Montmorillonite	26	5-1	Very Good	3	1960	4800	5100
Montmorillonite	23	5-2	Fair	5	1890	6000	6200
Montmorillonite	11	5-3	Very Good	1	3180	4500	5300
Montmorillonite	21	5-4	Fair	5	2430	7700	8000
Montmorillonite	24	5-5	Fair	4	2680	7600	7900
Montmorillonite	20	5-6	Good	1	3780	5400	6300
Illite	35a	6-1	Good	1	2010	2800	3400
Illite	36	6-2	Good	5	1780	5600	5800
Illite		6-3	Very Good	5	1720	5500	5700
Illite		6-4	Fair	3	2160	5300	5600
Illite-montmor.	42	6-5	Good	5	1720	5400	5600
Illite-montmor.	32	6-6	Good	5	2360	7500	7700
Illite-montmor.	31	6-7	Very Good	5	1410	4500	4600

DISCUSSION OF RESULTS

Average particle diameters and particle size distributions have been obtained for the majority of the clays studied. For the most part these were found to have particles from .1 to 1 micron in diameter. The reliability of the method for such comparatively large particles is not known, but examination of carbon blacks, whose sizes could be checked by electron microscopy, indicated the method to be satisfactory for particles under 1000 Angstroms in diameter. Since for the clays the shape factor used was $v=0$, nothing can be said about the particle thickness other than that it is much less than the diameter.

Kaolinites. The scattering curves of the kaolinites were difficult to interpret, possibly due to an erratic distribution of sizes. The curve obtained for a kaolinite from Murfreesboro, Arkansas was especially poor. However a match obtained for the lower part of the curve gave an average particle diameter of 750 Å, in agreement with the value of 500–1500 Å obtained by Kerr *et al.* (1950a) from electron micrographs. No match could be obtained for the kaolinite from Bath, South Carolina, but the other three kaolinites examined gave average particle diameters from

2500 to 3200 Å. All of the matches were with theoretical curves having n=1, indicating a wide range of sizes, a fact also in agreement with electron microscopy.

Dickite. Only one dickite was examined and this gave an average particle diameter of 4300 Å. Electron photomicrographs from Kerr *et al.* (1950a) show this sample to consist chiefly of very large euhedral flakes up to 47,000 Å in diameter, with a lesser amount of fine material. It seems probable that such large flakes would contribute very little to the small-angle scattering in the angular range examined, and that the results obtained are a measure of the finer material with a contribution from the thickness of the large flakes.

Montmorillonites. The montmorillonite samples gave average particle diameters ranging from 4500 to 8500 Å, most of them with rather narrow size ranges. West (1952) found the particle sizes of montmorillonites to lie in the range .3 to .7 microns (3000–7000 Å) but his small-angle scattering method made no allowance for particle shape, treating the samples as assemblages of spheres. Kahn (1959) in an examination of a montmorillonite from Clay Spur, Wyoming by electron microscopy found that the particles had "major dimensions" from 2800 to 13,800 Å. In this study, a similar sample had an average diameter of 5100 Å.

Illites. The illite samples gave average particle diameters ranging from 3000 to 6000 Å, all but one having narrow size distributions. Kahn (1959) found that the API#49 illite from Fithian, Illinois had "major dimensions" of 1000 to 4800 Å by electron microscopy. This sample had an average diameter of 3400 Å in this study.

Interlayered Illites and Montmorillonites. Three samples of interlayered illite and montmorillonite gave average particle diameters of 5600 Å, 7700 Å and 4600 Å, all with narrow size distributions.

In conclusion it can be stated that particle size distribution for clay minerals can be extracted from small-angle *x*-ray scattering data by the Shull and Roess method. How reliable these results are is not known but where data are available for comparison, West (1952), Kerr *et al.* (1950a) and Kahn (1959), the results are similar.

ACKNOWLEDGMENTS

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