Clay Minerals (1993) **28**, 485–494

This and the following four papers were presented at a joint meeting of the Clay Minerals Group of the Mineralogical Society and the Particle Characterization Group of the Royal Society of Chemistry entitled "Characterization of Clay Particle Shape and Size" held on 8–10 April 1992.

SIZE AND THICKNESS MEASUREMENT OF POLYDISPERSE CLAY SAMPLES

B. R. JENNINGS

Research Department, ECC International Ltd, St Austell, Cornwall, and Chemistry Department, University of Bristol, UK

(Received 12 October 1992; revised 15 February 1993)

ABSTRACT: Measurement of clay particle size invariably presents data in the form of equivalent spherical diameters. For asymmetric particles the equivalent spherical diameter varies with the method of measurement. Based upon an understanding of the theoretical concepts involved, a method has been proposed whereby comparison of data on a given sample from two different techniques can reveal information about the minor dimension of the particle. Theoretical expressions are given for the equivalent spherical diameter of cylindrically symmetric rods and discs from which it is shown that some of the existing measurement methods are more dependent upon size than the degree of non-sphericity whilst for others the reverse is true. It is shown how for rods and discs one can obtain information on both an average axial ratio and the distribution of this parameter for heterogeneous samples. Illustrated data are given for three kaolin samples. Far from showing inconsistency between the variable spherical diameters yielded by different instruments, the data produce compatible size and thickness parameters which match those observed in supplementary, unreported electron microscope experiments. A method of measuring particle major and minor parameter distributions is indicated.

A variety of commercial and academic instruments exist for the measurement of particle size and size distribution (Barth, 1984; Miller & Lines, 1988; Allen, 1990; Syvitski, 1991). Owing to the complexity of the basic theory, it is usual to interpret experimental data in terms of equivalent spherical diameters (ESD). However, clay mineral particles are never spheres. Unlike colloids in general, minerals call for particle sizing methodology which can inherently embrace particle asymmetry. Whilst it is not possible to fully account for the indiscrete morphology of mineral particles, cylindrically symmetric rods and discs, which are extreme deviations from the sphere in one of the particle dimensions, are perhaps the most representative models to use. Furthermore, unlike the unidimensional sphere, these geometries are anisodiametric and require two parameters to characterize them, namely the major and minor dimensions. In addition, clay samples are never monodisperse, i.e. composed of particles of a single size species. Rather they are heterogeneous or polydisperse. Hence, interest centres on the ability to measure distributions in one or more of the characterizing parameters. Commercial sizing instruments are increasingly able to give the distribution of the equivalent spherical diameter. There is a growing need for the simultaneous measurement of the heterogeneity in particle thickness.

A variety of physical properties is measured as the basis of particle size analysis. A few might be appreciated from Fig. 1. Particle diffraction of a light beam relates to the average

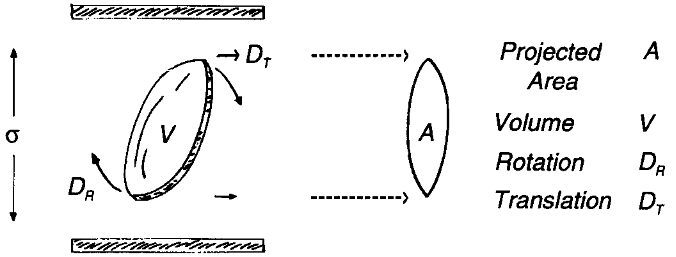

FIG. 1. Size measurement principles. Different methods depend upon the measurement of alternative physical parameters of the asymmetric particles.

projected area (A) of a particle if Frauhofer optics (Levi, 1986) are used to record the diffraction effects. This is the principle used in the Leeds and Northrup "Microtac", Malvern "2600" and the Coulter "LS" instruments. Alternatively with true Mie-theory angular scattering calculations (Mie, 1908), it is the particle volume (V) that is the fundamental parameter that gives rise to the measured positions of the diffraction rings. Methods based upon the detection of conductivity changes as particles pass between a pair of energized electrodes also indicate particle volume characteristics. This is the so called "Coulter" principle. Volume related instruments include the Malvern "Mastersizer" and the Coulter "Multisizer II". During recent years it has become popular to measure the fast, time-dependent fluctuations in the scattered intensity when observed at a fixed scattering angle. This is the so-called photon correlation scattering which depends upon particle Brownian motion. In this case the translatory diffusion coefficient (D_T) is the influential particle parameter, and the Malvern "Autosizer", Coulter "N-4" series and the Brookhaven "B1-90" are relevant commercial instruments. More recently, and of particular interest to the author, has been the measurement of particle rotary motion related to a rotary diffusion constant (D_R) in which external pulsed magnetic, electric or acoustic fields cause particles to rotate in the field and thereby modify specific optical properties. Commercial instruments are not available for this class. Automated systems have been described by Oakley *et al.* (1982) and by James (1987). Perhaps the best known method to mineralogists, however, is that of measuring the sedimenting characteristics of particles in a gravitational field. This is the principle of the "Sedigraph" and the feature of the individual particles is the Stoke's parameter. The Micromeritics "Sedigraph", Christisen Scientific "Fritsch Analysette" and the Brookhaven "Scanning Disc Centrifuge" are alternative commercial instruments.

For purely spherical particles the diameters from all methods should, in principle, equate. When the particles are asymmetric two important characteristics need to be appreciated. Firstly, for a given method of measurement one can calculate the diameter of the sphere that would respond in the observed manner and an equivalent spherical diameter (ESD) could be obtained. These spherical diameters will not equate between the various physical methods used. Secondly, as the various methods have different dependencies upon the non-sphericity (or axial ratio), one should be able to determine this axial ratio by comparing the results from two or more sizing methods. This is the basis of the present discussion. Equations are summarized for the ratio of the true major dimension of the particle to the ESD for each of the physical effects mentioned above. Equations have been condensed from the fuller theories of oblate and prolate spheroids (Parslow & Jennings,

1988) to the two cases of discotic and filamentous particles. The method of extracting axial ratio data for these two models is elucidated and typical data are given in terms of three samples of kaolin.

THEORETICAL RÉSUMÉ

Introduction

A summary of the equations is given for the limiting cases of rod-like particles of length l, thickness t and axial ratio ($\rho = l/t$) and for discotic particles of surface diameter δ, thickness t, and axial ratio ($\rho = d/t$). In each case ρ is assumed to be in excess of 10. Consideration is given to classes of measurement, via the basic size-related dependent parameter such as the particle volume, projected area, translatory diffusion coefficient, rotary diffusion coefficient and Stoke's parameter. In each class, it is assumed that all experimental factors have been considered and that fully corrected values of the equivalent spherical diameters (d_j) are available. The subscript j indicates a value derived from a method dependent upon the volume (V), area (A), Stoke's parameter (S) etc. The following equations give the ratio of the relevant d to the true major dimensional parameter for each of the physical factors in question.

Rod-like particles

The equivalent spherical diameter d_V for methods depending on the particle volume is given in terms of l and ρ by the expression

$$\frac{d_V}{l} = \left(\frac{3}{2\rho^2}\right)^{1/3} \tag{1}$$

The equivalent spherical diameter d_A for methods depending upon the measurement of the projected area of the particle is given in terms of the axial ratio as

$$\frac{d_A}{l} = \left\{\frac{1}{\rho}\left(1 + \frac{1}{2\rho}\right)\right\}^{1/2} \tag{2}$$

For sedimenting particles the equivalent spherical diameter d_S for a particle following equivalent friction motion under gravity is given by equation 3, whose

$$\frac{d_S}{l} = \frac{\sqrt{1{\cdot}5\ln(2\rho)}}{\rho} \tag{3}$$

In the case of translatory diffusion coefficients, the equivalent spherical diameter d_T is represented as follows

$$\frac{d_T}{l} = \left\{\frac{1}{\ln(2\rho)}\right\} \tag{4}$$

The equivalent spherical diameter from the interpretation for induced rotary diffusion is

$$\frac{d_R}{l} = \left\{3\ \ln(2\rho - 0{\cdot}5)\right\}^{-1/3} \tag{5}$$

In all cases, the various diameters d_j are all less than the true rod length and the ratio of d_j/l is a different fraction of axial ratio with each method. The ratios are expressed graphically in Fig. 2.

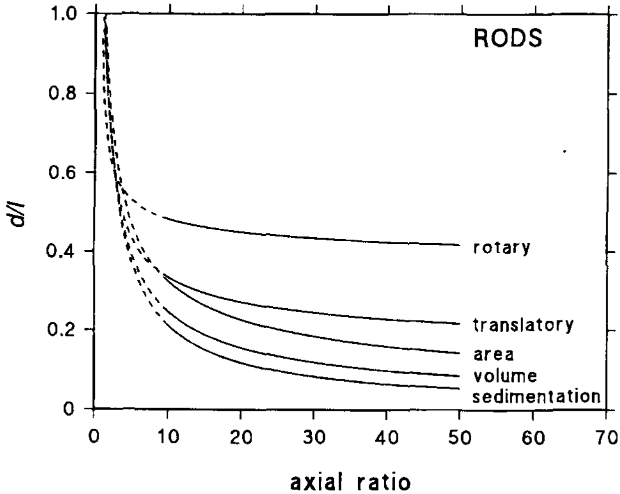

FIG. 2. Ratio of the equivalent spherical diameter (d) to a rod particle length (l). With non-spherical particles, the diameters vary with the physical entity being monitored.

Disc-shaped particles

In the case of the right symmetrical disc the equivalent equations are as follows for the volume equivalent spherical diameter.

$$\frac{d_V}{\delta} = \left(\frac{1\cdot5}{\rho}\right)^{1/3} \tag{6}$$

whilst the equivalent projected area for spherical diameter for discs is given by

$$\frac{d_A}{\delta} = \sqrt{0\cdot5 + 1/\rho} \tag{7}$$

For sedimenting discs the equivalent Stoke's spherical diameter is given by

$$\frac{d_S}{\delta} = \sqrt{\frac{1\cdot5}{\rho} \text{ arc tan } \rho} \tag{8}$$

The spherical diameter for an equivalent translating particle is as follows:

$$\frac{d_T}{\delta} = \frac{1}{(\text{arc tan } \rho)} \tag{9}$$

whilst that for freely rotating discs, the equivalent rotary motion is expressed as

$$\frac{d_R}{\delta} = (4/3\pi)^{1/3} \tag{10}$$

Graphs of the ratios expressed in these equations are given in Fig. 3.

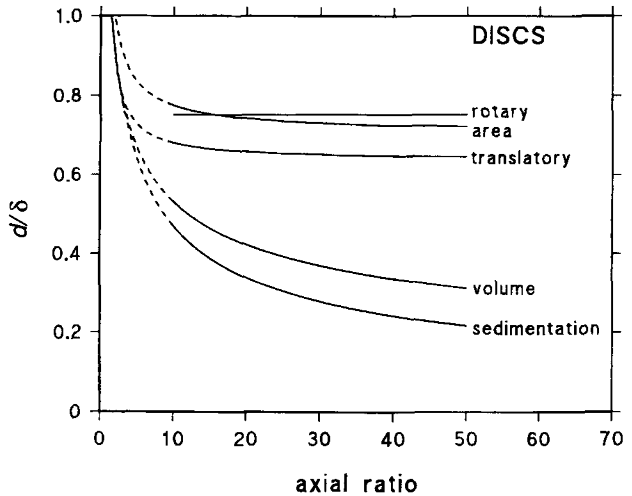

FIG. 3. Ratio of equivalent spherical diameters (d) to the major dimension (δ) for discs. Note the greater sensitivity of Stoke's diameter methods to variable particle shape.

TABLE 1. Comparison of ESD values (in μm) for (a) rods and (b) discs of 1 μm. Major dimension with $\rho = 10$.

	Rod ($l = 1$ μm)	Disc ($\delta = 1$ μm)
Volume (d_V)	0·25	0·53
Projected area (d_A)	0·31	0·77
Stoke's parameter (d_S)	0·21	0·47
Translatory diffusion (d_T)	0·33	0·68
Rotation diffusion (d_R)	0·48	0·75

Implications of equations

From the foregoing equations a number of factors are apparent.

(i) The various ESD exhibit significantly different dependency on axial ratio. Hence, different methods and commercial instruments do not give the same ESDs for asymmetric particles.

(ii) It is instructive to consider both rod and disc-shaped particles of 1 μm major dimension each with an axial ratio of 10. For such cases Table 1 and Fig. 4 illustrate the actual ESD which would be indicated by each of the relevant experimental methods. The relative size of the sedimenting sphere equivalent to the 1 μm rod is in reality only 0·21 μm. This is especially relevant in the clay mineral industry where screening is used to size-select material and where sedimentation-based instruments are used to measure percentages of material less than a specified size. The reality may be far from that quoted.

(iii) Methods such as those depending upon rotatory and translatory diffusion are less sensitive to axial ratio than those based upon the Stoke's diameter and the volume diameter measurement. All methods however are quite sensitive to axial ratios.

(iv) For a given particle size the ratio of any two ESD expressions within the series of equations 1 to 5 should depend uniquely upon the rod axial ratio. Similar reasoning applies to equations 6 to 10 for discs. A method for evaluating the axial ratio and hence the minor

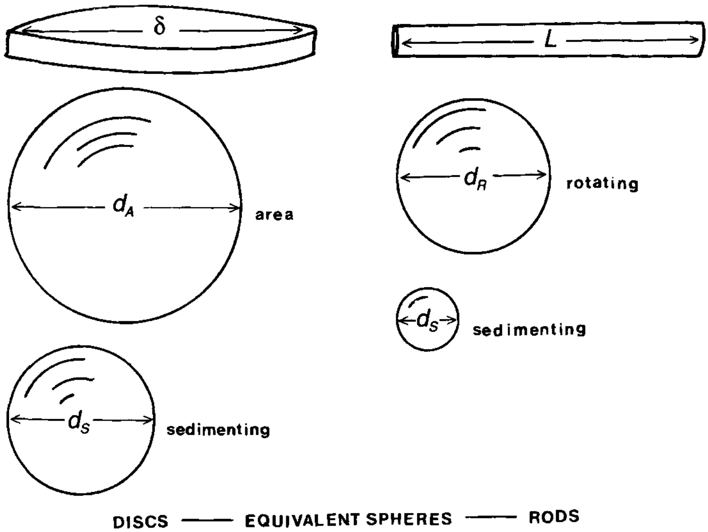

FIG. 4. Visualization of the equivalent sphere sizes to the true facial diameter and the length of discs and rods. The implication of this on the commercial screening of platey and fibrous material is apparent.

dimension is indicated via a comparison of the ESD data obtained from two or more instruments.

(v) The most precise measurement of particle size will be that which is least influenced by particle shape and axial ratio. This will be rotatory diffusion, followed by translatory diffusion and projected area measurements. Evaluation of volume equivalent diameters and Stoke's diameters will be the most sensitive to variation in particle shape. If particle size is determined independently, these methods should be the best to use in order to indicate shape and axial ratio.

(vi) A corollary to (v), however, is that the presence of ill-defined particles in an ensemble of particles with assumed geometric form, will have a greater distorting influence on sedimentation data than on translatory or rotary diffusion data.

(vii) The utility of the equations is as follows. With two types of apparatus available, the standard procedures are followed to obtain measurements of the distribution of particle ESD values by each method. It is convenient to express the data as weight cumulative distributions. One can then compare the two ESD values from the two methods at any chosen equivalent percentage point on the two distribution curves and calculate a value for the axial ratio. This is best achieved by generating the appropriate master curves of ratios of the relevant ESDs for the experimental methods used. For example, from equations 6 and 10, a master plot of the dependence of (d_V/d_R) upon axial ratio can be generated and used to interpolate comparable data from Mie scattering and rotary diffusion instruments to yield ρ values for discs. By considering Figs. 1 and 2, the greatest differential between methods is obtained in the ratio d_R/d_S. Hence, by way of illustration, equations 10 and 8 have been combined (or the values taken directly from the curves of Fig. 3) to draw the master plot of d_R/d_S for disc-shaped particles. From the experimental ESD, the theoretical curves (Fig. 5) can be used to give values of ρ directly at one or more points throughout the size distributions.

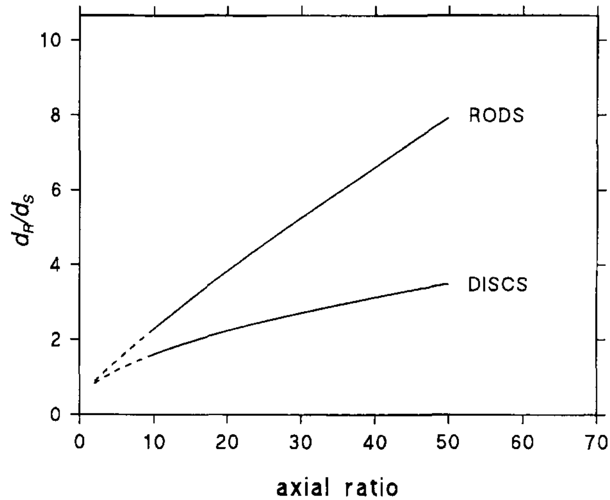

FIG. 5. Ratio of equivalent spherical diameters from rotary diffusion dependent (d_R) and sedimentation dependent (d_S) measurement procedures. Data are for disc and rod-shaped particles. For axial ratios of unity, the curves would come together at unit ratio.

(viii) To obtain values of the true dimension of rod lengths or disc diameters, the data for d_j and ρ can be reinterpreted via the relevant equations for the assumed model. Better still, the experimental raw data should be reinterpreted in terms of the equations for the true shape to give l (or δ) values directly. This is simpler using those methods which are less sensitive to axial ratio and shape variations.

REPRESENTATIVE DATA

Measurements on kaolin samples

Figure 6 presents the results of a study on three kaolin samples, all of middle Georgia, USA origin. Sample A is a well-delaminated clay, sample B is a beneficiated material and the sample C is a calcined kaolin. In each case measurements of the particle size distribution have been made using the electric birefringence method described elsewhere. Although it is equally convenient by this method to express data in disc diameters, distributions have been presented for the equivalent log-normal ESD distribution for rotating equivalent spheres. The graph also displays experimental Sedigraph measurements—relating to Stoke's diameters for the three samples. An advantage of the Sedigraph method is that it gives continuous distributions, whilst to date, the simplified birefringence method force-fits the data to a log-normal distribution.

For each sample, the two sets of data have then been compared at the central or 50% cumulative point for which the subscript 0·5 has been used. From the ratio of the birefringence and the sedimentation values, a theoretical graph of d_R/d_S *vs.* ρ was used to obtain a value for ρ using this axial ratio. With this axial ratio it was then possible to generate the equivalent Stoke's ESD distribution based upon the rotary birefringence measurements. These are the broken curves shown in Fig. 6.

The following factors are apparent from the data. Firstly, whereas hitherto it might have been thought that rotary birefringence and Stoke's Sedigraph data are incompatible, in

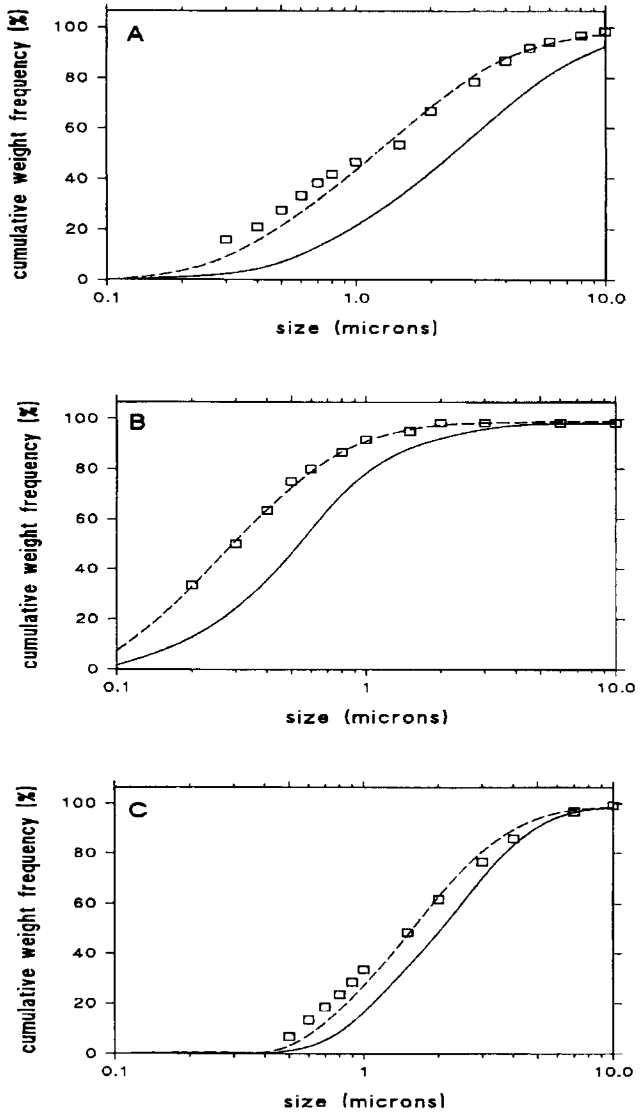

FIG. 6. Positive cumulative distributions for three samples of the tabular mineral kaolin. Full curves are for the rotary equivalent spherical diameter (d_R) and data points are for sedimenting equivalent spheres (d_S). The broken curve is for the (d_R) data, converted to (d_S) values using the theory presented herein. Frames A, B and C are for a delaminated, a beneficiated and a calcined clay, respectively.

reality this is not so. The explanation of the difference is apparent in terms of axial ratio dependence. Secondly, based upon the mid-point the following values of axial ratio were obtained. For delaminated plates $\rho = 13$; for the beneficiated sample $\rho = 8{\cdot}5$ and for the calcined material $\rho = 4{\cdot}5$. Thirdly, the displacement between the Stoke's ESD and the rotary ESD curve is a measure of the non-sphericity of the material. Hence the calcined material most closely approximates a more isotropic overall shape whilst the delaminated material exhibits the greatest anisodiametric geometry. This is as expected. It is interesting

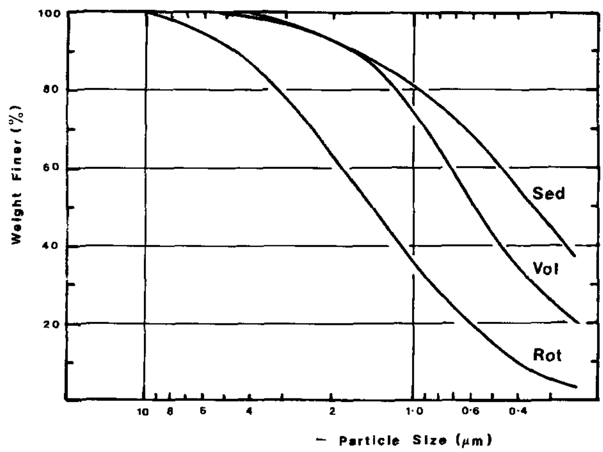

FIG. 7. Reversed cumulative distributions of the equivalent spherical diameters. Data for a single, fine kaolin sample, measured by three procedures. The keys Sed, Vol and Rot indicate data for d_S, d_V and d_R, respectively.

to note that in sample B which contains booklets, the data for the large particle sizes indicate that the sedimentation and the rotary data come together in this size range, consistent with the more spherical geometry of these stacks.

Finally it is interesting to compare the true disc size values with the ESD Sedigraph values. For the delaminated sample A, the 50% cumulative factor for the disc diameter distribution corresponds to a diameter of 3·7 μm and the calcined clay would have a value of 2·7 μm. In each case this is twice the size indicated by the Sedigraph ESD data.

COMPARISON OF DATA FROM VARIOUS INSTRUMENTS

In Fig. 7 reversed cumulative weight size distributions are given for a relatively well delaminated, fine kaolin sample. Measurements were made on a Sedigraph, a Coulter counter type instrument giving volume related data and by electric birefringence depending upon rotary diffusion coefficients. At first sight it might be concluded that the three instruments are incompatible and that particle size distribution data are incomparable between instruments. In reality these three sets of data are compatible and illustrate the theory for discs in an interesting manner.

Firstly, it is to be noted that the data correspond to increasing ESD size in the sequence sedimentation to volume to rotary diffusion. When taken at the 50% weight cumulative point, one obtains $(d_S)_{0\cdot5} = 0\cdot35$ μm; $(d_V)_{0\cdot5} = 0\cdot6$ μm; and $(d_R)_{0\cdot5} = 1\cdot4$ μm. On the assumption that particles are best represented by right circular discs, comparison between d_R and either or both d_S and d_V should lead to axial ratio data. From the above $(d_R/d_S)_{0\cdot5} = 4\cdot0$ so that from equations 8 and 10 the axial ratio $\rho = 41$. Alternatively the ratio $(d_R/d_V)_{0\cdot5} = 2\cdot3$ which, in terms of equations 6 and 10 indicates $\rho = 43$. These are remarkably consistent and enable a value of $\rho = 42$ to be used. A comparison of d_V with d_S is obviously an insensitive exercise owing to the theoretical closeness of the two curves (Fig. 3). Highly delaminated material is indicated.

Finally, for this sample, it is of interest to compare the three ESD distributions and to seek the meaningful single distribution that best describes the sample geometry. This can be

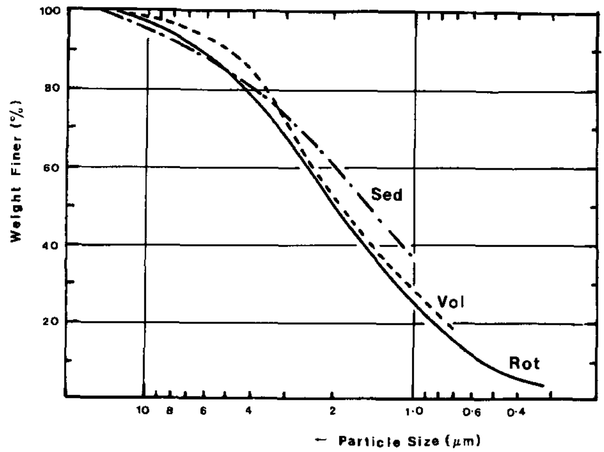

FIG. 8. Distributions for disc model diameters. These are the data of Fig. 6 after evaluating an average axial ratio and reinterpreting each set in terms of a disc model. Note the relative compatibility.

done in principle by generating values of δ from the ESD using the axial ratio found above. From the 50% cumulative weight point one can redefine the various d_j and $j = V, S$ or R using the appropriate asymmetry functions of equations 6, 8 and 10 to obtain a value of $\delta_{0 \cdot 5}$. In this example using values from d_V, d_S and d_R leads to values for $\delta_{0 \cdot 5}$ of 1·8 μm, 1·5 μm and 1·9 μm, respectively. Hence the three distributions come closely together in an approximate distribution for the disc geometry with a 50% cumulative weight point at ~1·8 μm as shown in Fig. 8.

ACKNOWLEDGMENT

The assistance of Dr N. Elton of ECCI in generating some of the curves is appreciated.

REFERENCES

ALLEN T. (1990) *Particle Size Measurement.* Chapman & Hall, London.

BARTH H.G. (Ed.) (1984) *Modern Methods of Particle Size Analysis.* Wiley Interscience, New York.

JAMES R.O. (1987) Rapid measurement of magnetic pigment particle size by transient magnetic birefringence methods. *Colloids Surfaces* **27,** 133–158.

LEVI L. (1986) *Applied Optics,* Vol. **1,** 77–78. Wiley, New York.

MIE G. (1908) Optics of turbid media. *Am. Physik* **25,** pp. 377–445.

MILLER B.V. & LINES R. (1988) Recent advances in particle size measurements: A critical review. *CRC Critical Reviews in Analytical Chem.* **20,** 75–116.

OAKLEY D.M., JENNINGS B.R., WATERMAN D.R. & FAIREY R.C. (1982) An electro-optic birefringence fine-particle sizer. *J. Phys. E. (Sci. Intrum.)* **15,** 1077–1082.

PARSLOW K. & JENNINGS B.R. (1988) Particle size measurement: the equivalent spherical diameter. *Proc. Roy. Soc.* **A419,** 137–149.

SYVITSKI J.P.M. (1991) *Principles, Methods and Applications of Particle Size Analysis.* Cambridge University Press, Cambridge.