
British Standards Methods for Determination of particle size distribution

Part 6. Recommendations for centrifugal liquid sedimentation methods for powders and suspensions

Méthodes de détermination de la granulométrie

Partie 6. Méthodes de sédimentation liquide centrifuge des poudres et
suspensions — Recommandations

Verfahren zur Bestimmung der Korngröße

Teil 6. Empfehlungen für die Sedimentation von pulverförmigen Stoffen und
Suspensionen in Flüssigkeiten nach dem Fliehkraftverfahren

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Foreword

This Part of BS 3406, prepared under the direction of the General Mechanical Engineering Standards Committee, is one of a series that describes recommended methods for determining particle size distribution and is based on methods which have come into more widespread use since BS 3406 : Parts 1 to 4 were first published in 1961 and 1963. Current and proposed Parts of BS 3406 are as follows:

- *Part 1 Sub-division of gross sample down to 0.2 mL
- Part 2 Recommendations for gravitational liquid sedimentation methods for powders and suspensions
- Part 3 Air elutriation methods
- *Part 4 Optical microscope method
- Part 5 Recommendations for electrical sensing zone method (the Coulter principle)
- Part 6 Recommendations for centrifugal liquid sedimentation methods for powders and suspensions
- †Part 7 Light scattering by single particles

Representative sampling and correct dispersion of particulate material are pre-requisites for the determination of size distribution, especially when using methods in which the test portion may be relatively small in amount. The procedures described in BS 3406 : Part 1 have been selected to give a test sample representative of the bulk sample.

No single method of size analysis can be specified to cover the many different types of powder encountered, but it is possible to recommend procedures that may be applied to the majority of cases. The purpose of these standards is to obtain uniformity in procedure for any method selected, in order to facilitate comparisons of size analyses made in different laboratories.

The choice of the most suitable method will depend on the following considerations:

- (a) the purpose for which the analysis is required, e.g. quality control, research, specification requirements;

- (b) the size range and other properties of the particles, e.g. density, solubility, refractive index;
- (c) the agglomeration and dispersion characteristics of the powder;
- (d) the amount of material available for analysis;
- (e) the method by which the sample has been collected;
- (f) the conditions in which the powder will be used, for example the state of dispersion in the test should be related to the state of dispersion in the application;
- (g) resources available.

The optical microscope method is the only method in which direct observation is made of the size and shape of the particles. Most other methods of particle size measurement ascribe a single dimension to each particle, usually expressed as the diameter of the spherical particle equivalent to some aspect of its properties, such as volume, surface, settling velocity or light scattering phenomena. Physical properties of the particles, such as solubility, friability, refractive index and conductivity, preclude the use of some methods. Nevertheless the same powder can be analysed using a range of techniques and if different size parameters are determined different size distributions will result. The intercomparison of results can only be reliable if each laboratory is using a representative sample and is measuring the same parameter by reliable equipment and procedures.

Since the particle size-dependent properties measured are different for the various techniques the resulting size analysis made on identical powders will also differ, the differences increasing with increasing irregularity of particle shape. It is therefore essential when reporting an analysis that the method used should be named. Good reproducibility or relative precision does not necessarily imply accuracy.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

*Under revision.

†In preparation.

Section one. General

1 Scope

This Part of BS 3406 describes four centrifugal liquid sedimentation methods for the determination of the particle size distribution of powders and suspensions, particularly those with a maximum size of about 5 µm:

- (a) the X-ray centrifuge method;
- (b) the pipette centrifuge method;
- (c) the photocentrifuge method;
- (d) the decantation centrifuge method.

Appendix A provides information on liquid suspending media.

NOTE 1. The X-ray centrifuge method is described first, because the inner radius of the suspension is fixed, the theory is simple, and the mass distribution is directly obtained.

With the pipette centrifuge, the inner radius increases with each sample extraction, leading to a more complex theory. The mass distribution is determined directly.

With the photocentrifuge, the radius is also fixed but the distribution is nominally a surface one when the homogeneous technique is used. The relationship is not a direct one, due to the complexity of the particle/light interaction, so the technique can be only used to compare similar material. With the line start technique the distribution obtained is nominally a mass one but the limitations and restrictions that apply to the homogeneous techniques are still valid.

The decantation centrifuge operates as a line start technique and the supernatant suspension, containing the undersize fraction, is removed to obtain a single point on the distribution curve. By carrying out multiple analysis a full distribution is obtained. The instrument can also be used as a photocentrifuge.

In all four methods the centrifuge bowl consists of a hollow cylinder with a circular aperture at the centre of one face through which the suspension can be fed into the rotating bowl.

NOTE 2. The titles of the publications referred to in this standard are listed on the inside back cover. A bibliography of relevant publications is given in appendix B.

2 Definitions

For the purposes of this Part of BS 3406 the definitions given in BS 2955 apply, together with the following.

2.1 spatulation. The process of working and kneading gently with a flexible spatula after the addition of a few drops of dispersant.

2.2 homogeneous suspension. A suspension in which the particles are uniformly dispersed in the sedimentation liquid.

2.3 line start technique. A technique in which a thin layer of homogeneous suspension is floated on the surface of the sedimentation liquid.

2.4 immersed density. The mass of powder per unit volume of suspension medium that it displaces.

3 Principles

Centrifugal liquid sedimentation methods are classified as either incremental or cumulative, line start or homogeneous, as are the gravitational liquid sedimentation methods recommended in BS 3406 : Part 2.

Centrifugal liquid sedimentation methods are used because most gravitational sedimentation techniques have limited worth for particles smaller than about 2 µm to 3 µm, depending on the settling times involved and, in addition, suffer from the effects of convection, diffusion and Brownian motion which often result in the measured size distribution being finer than the actual distribution. These difficulties may be reduced by speeding up the settling process by centrifuging the suspension.

Calculations of size distributions from centrifugal data are more difficult than calculations from gravitational data since particle velocities increase as they move away from the axis of rotation. That is, the velocity of a particle depends on its position in the sedimenting suspension as well as on its size, whereas for gravity sedimentation the settling velocity is dependent solely on size. One method of overcoming this difficulty is to use the line start technique so that all particles of the same size are in the same radial position in the centrifugal field and, hence, have the same velocity.

Readings should not be accepted within the first minute of the analysis as turbulence is set up when the suspension is introduced into the spinning centrifuge. It is inadvisable to run the centrifuge for more than about 2 h because of the effects of convection currents, diffusion and Brownian motion.

4 Calculation

4.1 Calculation of particle size

4.1.1 General. The calculation of settling velocity is dependent on Stokes' law which may conveniently be stated in the following form:

$$d_{St} = \left(\frac{18\eta}{(\sigma-\rho)\omega^2 r} \frac{dr}{dt} \right)^{1/2} \quad (1)$$

where

d_{St} is the Stokes diameter, defined as the diameter of a sphere which has the same immersed density and the same free falling velocity in a given fluid as the particle within the viscous flow region; the Reynolds number should not exceed 0.25 if the error in Stokes diameter is not to exceed 3 %;

η is the absolute viscosity of fluid;

σ is the immersed density of particle;

ρ is the density of fluid;
 r is the distance of the particle from the axis of rotation of the centrifuge bowl;
 $\frac{dr}{dt}$ is the settling velocity of the particle;
 ω is the speed of rotation of the centrifuge in rad/s.

4.1.2 Line start techniques. If the surface of the suspension is at radius S , the largest size present at measurement radius R at time t may be determined by integrating equation (1) to give:

$$d_{St} = \left(\frac{18\eta \ln(R/S)}{(\sigma - \rho)\omega^2 t} \right)^{1/2} \quad (2)$$

For incremental techniques R is the radius of the measurement zone. For cumulative techniques R is usually the internal radius of the bowl.

4.1.3 Homogeneous technique. The size of the largest particle present in the measurement zone at radius R is given by equation (2). Particles of size d_i will have originated from radius r_i where:

$$d_i = \left(\frac{18\eta \ln(R/r_i)}{(\sigma - \rho)\omega^2 t} \right)^{1/2} \quad (3)$$

4.2 Calculation of frequency distribution

4.2.1 General. The method of calculation depends both on the technique and the mode of operation.

4.2.2 Incremental techniques using a line start. Calculation of the frequency distribution is simple since the concentration of particles in the measurement zone at depth h and time t , $C(h, t)$, is directly proportional to the fractional mass of particles of size d_t (the mean size of particles in the measurement zone at time t , calculated using equation (2)). Values of concentration plotted against d_t represent a mass frequency curve which, if integrated by area, yields cumulative frequency by mass data.

4.2.3 Incremental technique with homogeneous suspension. For gravity sedimentation the fractional concentration of particles in the measurement zone at depth h and time t , $C(h, t)$, is directly proportional to the cumulative mass F_n smaller than the Stokes diameter, d_{St} .

$$F_n = \int_0^{d_{St}} F(d) dd = C(h, t) \quad (4)$$

For centrifugal sedimentation a direct proportionality does not exist since the particles move in radial paths and thus the interparticle distance increases as they move outwards.

Particles originating at radius r_i in an annular element of thickness δr_i will occupy an annular element of thickness δR at the measurement radius R . The relationship between F_n and the measured concentration, C , at radius R is:

$$F_n = \int_0^C \left(\frac{r_i}{S} \right)^2 dC \quad (5)$$

The general solution is:

$$F_i = (1/2)(y + y_{i-1,j})C_i + \sum_{j=1}^{i-1} \left(\frac{y + y_{j-1,j}}{y_{j+1,j} + y_{j,i}} - \frac{y + y_{i-1,j}}{y_{j,i} + y_{j-1,j}} \right) F_j \quad (6)$$

where

$$y = \left(\frac{R}{S} \right)^2 \quad (7)$$

$$y_{i,j} = y (d_i/d_j)^2 \quad (8)$$

$$i = 1, 2, 3, 4 \dots m : y_{0,i} = 1.$$

Equation (6) is a set of linear equations which express the desired values of F_i explicitly in terms of the measure values of C_j . The coefficients in the equations depend on the ratios of the values of d_j (corresponding to the ratio of measurement times).

Consequently, if these are chosen in a geometric sequence the coefficients are considerably easier to calculate and the equations themselves are also simplified. The coefficients depend also on the dimensions of the centrifuge bowl and the amount of suspension.

A time ratio of 2:1 is recommended giving a diameter ratio of $\sqrt{2}$:1. The modified form of equation (6) becomes:

$$F_i = (1/2)(y + y^{1/2})C_i + \quad (9)$$

$$+ \sum_{j=1}^{i-1} \left(\frac{1}{y^{(1/2)(i-j-1)} + y^{(1/2)(i-j)}} - \frac{1}{y^{(1/2)(i-j)} + A} \right) F_j$$

where

$$A = 1 \text{ for } j = 1 \quad (10)$$

$$A = y^{(1/2)(i-j+1)} \text{ for } j \neq 1$$

when

$$i = 1, \quad (11)$$

$$F_1 = (1/2)(1 + y)C_1$$

5 Size limits

The upper size limit by centrifugal sedimentation is fixed only by the unreliability of measurements taken in the first minute of the analysis. Broadly, gravitational sedimentation can be used down to about 2 μm to 3 μm whereas centrifugal analysis is used up to about 5 μm , but this limit can be extended considerably, if desired, by using a more viscous liquid and/or slower centrifuge speeds.

A lower size limit (d_{min}) under ideal vibration-free, constant temperature, conditions can be estimated as follows.

The radial displacement by Brownian motion of particles during the sedimentation should be much less than the displacement due to the centrifugal field, i.e.

$$\Delta r^2 \ll (R - S)^2 \quad (12)$$

If the root mean square Brownian displacement is to be a fraction f_1 of the sedimentation distance $(R - S)$, the following relationship can be derived*.

$$d_{\min} = \left(\frac{12kT}{\pi} \frac{\ln(R/S)}{(\sigma - \rho)\omega^2(R-S)^2 f_1^2} \right)^{1/3} \quad (13)$$

An alternative criterion is to find the size d such that the variation in size due to Brownian motion is less than some fraction f_2 of the calculated size, i.e.

$$\Delta d \ll f_2 d$$

This leads to the expression:

$$d_{\min} = \left(\frac{3kT}{\pi(\sigma - \rho)\omega^2 R^2 \ln(R/S) f_2^2} \right)^{1/3} \quad (14)$$

Taking typical values, for example:

Boltzmann constant, $k = 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$;

Absolute temperature, $T = 300 \text{ K}$;

$R = 0.07 \text{ m}$;

$S = 0.04 \text{ m}$;

$(\sigma - \rho) = 1500 \text{ kg} \cdot \text{m}^{-3}$;

$\omega = 25\pi \text{ s}^{-1}$;

A maximum value of 0.05 is recommended for f_1 , making $d_{\min}$ in this example equal to $0.075 \mu\text{m}$ and f_2 equal to 0.02.

Apart from the variation in particle size at the sampling level due to Brownian motion (f_2), the resolution of the system will be affected by the depth of the sampling zone. If this depth is Z and the particle size gradient is dd/dr , the variation of size across the zone will be $Z(dd/dr)$.

For a centrifuge system:

$$\left(\frac{dd}{dr} \right)_{r=R} = \frac{d}{2R \ln(R/S)}$$

and putting $Z = f_1 (R - S)$,

the size variation will be:

$$\frac{f_1 (R - S)d}{2R \ln(R/S)} \quad (15)$$

Hence, for the preceding experimental data:

$$\text{fractional size variation} = \frac{f_1 (R - S)d}{2R \ln(R/S)} = 0.383 f_1$$

The reciprocal of this quantity will be a measure of the resolution of the system.

The values $f_1 = 0.05$ and $f_2 = 0.02$ ensure that the system resolution is not adversely affected by Brownian motion.

6 Concentration effects

Stokes equation applies to the sedimentation of a single spherical particle settling infinitely slowly in a fluid of infinite extent. This requirement is never fulfilled in sedimentation analysis where particles are separated by a finite distance and mutually affect each other and are also

affected by neighbouring surfaces. In order to reduce these effects as far as possible, low concentrations should be used. A recommended upper volume concentration for a homogeneous technique is 0.2 % and the distance between walls in contact with the suspension should be at least 0.5 cm to reduce wall effects to an acceptable level. Duplicate analyses should be carried out at two different concentrations in order to determine whether the concentration effects are negligible.

7 Suspension and dispersion

7.1 Selection of suspending liquid

The powder may not form a good dispersion in the suspending liquid alone, in which case a suitable dispersing agent is necessary. This agent may be incorporated in the suspending liquid or added directly to the powder. It is essential that the liquid suspending medium satisfies the following.

- The particles should not dissolve or change chemically in the liquid and should also not swell or contract.
- The liquid should inhibit the formation of agglomerates during sedimentation. This may often be achieved only by the addition of wetting or dispersing agents. (See appendix A.)
- It is essential that the density of the liquid is less than the immersed density of the particle. If the difference between the density of the particles and the density of the liquid is less than 500 kg/m^3 , it is essential that special care is taken to avoid convection currents.
- It is essential that the viscosity of the liquid is selected so that, on the one hand, the analysis does not take so long that thermal instabilities arise and, on the other hand, the coarsest particles do not settle so rapidly as to make the estimation of settling time too imprecise.

Appendix A gives a summary of sedimentation liquids and dispersing or wetting agents for various solids. This table is for guidance only and it is recommended that the suitability of a particular system be ascertained as indicated in 7.2 and 7.3.

7.2 Tests for dispersion

7.2.1 General. One of the tests as detailed in 7.2.2, 7.2.3 or 7.2.4 should always be carried out and it is recommended that as the test in 7.2.5 takes a good deal of time this test should only be carried out on major test series with similar systems.

7.2.2 Microscopical examination. A small drop of the suspension as prepared in the sedimentation apparatus, at the concentration to be used, is placed on a microscope slide without a cover glass. Examination of all parts of the slide under an adequate magnification will show the particles to be entirely separate and free from each other in a good dispersion, or will show characteristic chains and aggregates of particles in a poorly dispersed or flocculated suspension.

*Brugger, K, *Powder Technology* (1976) 14, 187–188.

Unless extreme care is taken with suspensions in mobile liquids, lowering of a cover slip on to the suspension will cause separation of different particle sizes and this will give a false idea of the degree of dispersion.

The microscope test is not a guarantee of an agglomerate-free suspension.

7.2.3 Qualitative sedimentation (preliminary observations). Suspensions of the powder (approximately 0.2 % by volume but in concentration not less than that to be used in the particle size analysis) are prepared in the selected liquid, and their behaviour is observed on centrifuging. Good dispersions settle out less rapidly than suspensions which are wholly or partly flocculated and show no sharp line of demarcation between clear liquid and the turbid lower layers as settling proceeds.

7.2.4 Photometric measurement. Since the optical density of a suspension immediately after agitation is a measure of the surface area of the suspended particles, photometric measurement may be used to determine the efficacy and optimum concentration of dispersing agents.

7.2.5 Quantitative sedimentation (tests on final dispersion). Several sedimentation analyses should be carried out:

- (a) using different sedimentation liquids;
- (b) using different dispersing or wetting agents;
- (c) having different solid concentrations;
- (d) with different sedimentation distances.

A test of good dispersion and freedom from mass convection effects is that the proportion of undersize should not be significantly decreased by increasing the concentration of powder by a factor of 2. If this condition does not hold the recommended volume concentration of 0.2 % may be too high.

7.3 Preparation for a sedimentation analysis

Select a suspending liquid (see appendix A). If not already known, determine the viscosity of the selected suspending liquid at the analysis temperature.

Determine the density of the liquid at the analysis temperature and the immersed density of the particles in the sedimenting liquid in accordance with BS 733. The amount of material available is generally greater than the amount needed for the analysis. A representative test portion should therefore be obtained from the laboratory sample (see BS 3406 : Part 1). The whole of the test portion should be used in the subsequent analysis.

The upper size limit for most centrifugal sedimentometers is normally about 5 μm . For homogeneous sedimentation it

is necessary for the bulk of the powder to either settle out (cumulative techniques) or reach the measurement zone (incremental techniques). This may require a higher centrifuge speed, a lower viscosity liquid or protracted analysis time, each of which reduces the upper size that can be measured. If the whole size range is required, the coarse end can be analysed by gravity sedimentation and the two analyses combined. For homogeneous systems the 100 % value may be calculated from the mass of sample used or from concentration measurements, preparatively to introducing the suspension into the centrifuge bowl.

At the stage at which the test portion is to be wetted, slowly add the dispersing solution or liquid, work with a spatula to a paste and then a liquid suspension, taking care to avoid grinding the sample. If the suspending liquid does not readily wet the powder, add a drop or two of a wetting agent to the dry test portion. Make up to an appropriate volume for the apparatus to be used. Either shake or stir and, if necessary, treat with ultrasonics. De-aerate under reduced pressure if necessary. Select the duration and intensity of dispersing so that unwanted agglomerates are destroyed but any aggregates which are desired are not damaged. Energetic processes which damage the particles should not be used for dispersion.

8 Tests in duplicate

Carry out tests in duplicate on representative test portions taken from the same laboratory sample. Accept the results only if the proportions by mass less than the same Stokes diameters do not differ by more than 4 %.

9 Report

Plot the results of the analysis with the Stokes diameter as abscissae and the cumulative mass percentages as ordinates. Select from the smooth curve drawn through the points cumulative mass percentages corresponding to the series required. Report to the nearest 0.1 %.

The report should indicate which method has been used and should also state:

- the suspending liquid, its temperature, density, viscosity and volume used;
- the dispersing agent and its concentration;
- the powder, its mass and its density;
- method of dispersion.

Section two. The X-ray centrifuge method

10 Principle

With X-rays, mass concentration of an initially homogeneous suspension is determined without disturbing the suspension. The X-rays, after passing through the suspension, are detected by a scintillation counter. The signal from the counter is amplified, fed to a ratemeter and a trace is recorded by a pen recorder.

The attenuation of the X-ray beam is proportional to the atomic mass concentration of the suspension at the measurement radius.

$$I = I_0 \exp (-BC) \quad (16)$$

where

I is the intensity of the emergent beam with suspension in the centrifuge bowl;

I_0 is the intensity with suspending liquid in the bowl;

C is the concentration of powder in the beam;

B is a function of the atomic number of the elements in the beam.

The X-ray density (D) is defined as:

$$D = BC \log_{10} e \quad (17)$$

That is:

$$D = \log_{10} \left(\frac{I_0}{I} \right) \quad (18)$$

Materials having an atomic number less than about 13 are not sufficiently X-ray opaque for reasonable resolution and even at this level a volume concentration of more than 3 % is required to obtain a resolvable trace. In order to obtain a

resolvable trace a decrease in intensity of about 20 % is required when the suspending liquid is replaced by suspension. The trace produced as X-ray intensity against time is converted to mass undersize against diameter.

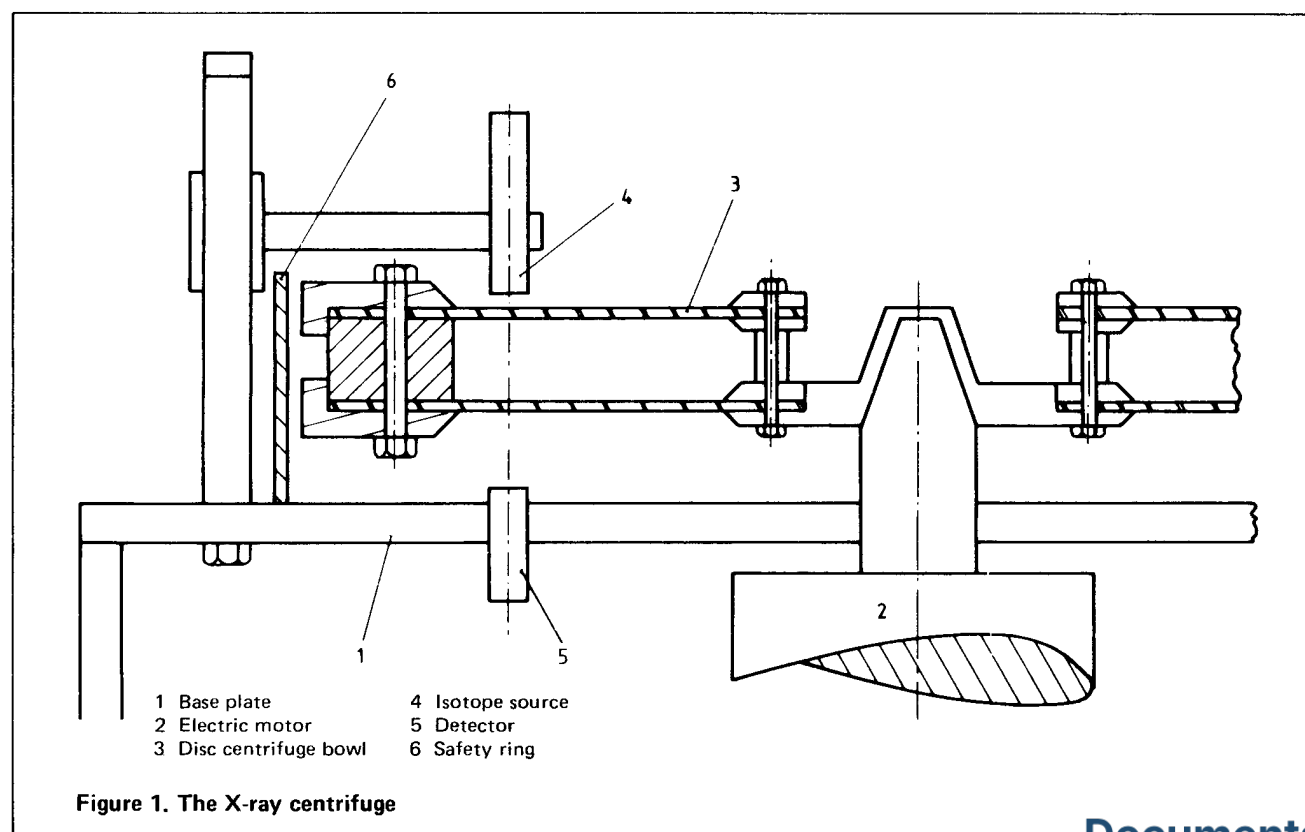
11 Apparatus

The X-ray centrifugal sedimentometer consists of a centrifuge body and associated electronics. The centrifuge itself (see figure 1) comprises the bowl (3) which is mounted directly on to the shaft of an electric motor (2), the base plate (1), the source and detector holders (4) and (5).

The base plate is mounted on a housing which absorbs the radiation that escapes from the measurement zone and on which the controls for the motor are fastened. A small axial fan mounted on the housing reduces heat convection from the motor to the bowl. The bowl is mounted horizontally and is surrounded by a metal safety ring (6). It is driven by a two-speed induction motor; 750 r/min and 1500 r/min are suitable speeds.

The X-ray beam emitted for the isotope source is collimated by narrow aperture lead slits in front of the source and detector; a width of 2 mm and an arc length of 10 mm are suitable. A scintillation counter is used as a detector; the signal from this is fed to a pre-amplifier, amplifier, ratemeter and recorder.

The ratemeter features a zero suppression control, which, together with a range switch, makes it possible to enlarge the output. A range of available time constants facilitates smoothing of statistical fluctuations in the output.



12 Preparation

12.1 Analysis sample

Make up an analysis sample (normally 100 cm³) as described in 7.3 to give a concentration of about 0.2 % by volume.

12.2 Temperature

Determine and record the temperature of the suspension.

13 Procedure

First fill the bowl with clean liquid and set up the electronics with the source in position and the bowl spinning.

Record the emergent intensity, I_0 , with clean liquid in the bowl. Select a suitable range (a magnification of 1, 3 or 10) depending on the mass absorption coefficient of the material under examination and suppress the zero to obtain a signal on the recorder. Move the arm with the source to the rest position while the bowl is emptied. Then spin it to the required speed, swing back the arm to the original position and pour the suspension into the bowl through the central opening using a funnel. The filling usually takes about 5 s. Switch on the recorder drive when filling is completed.

The trace starts dropping immediately because of the continuous dilution occurring at every point in the suspension due to radial settling. The run may be terminated when the signal has fallen to less than 10 % of its original value. For a fully automated evaluation, the signal from the instrument can be recorded on a magnetic tape which is then fed to a computer.

14 Calculation of results

14.1 Calculation of Stokes diameters (only necessary when operating manually)

The Stokes diameter for a time of 1 min is determined using equation (2). At times in a two-to-one progression subsequent diameter values will be in a one-to-root-two progression.

14.2 Calculation of cumulative percentage undersize (only necessary when operating manually)

The following form of equation (18) is used:

$$B'C = \log_{10} \left(\frac{L_0}{L_0 - L} \right) \quad (19)$$

where

L_0 is the recorder signal with clear liquid in the sedimentation vessel;

L is the signal with suspension in the vessel;

$$B' = B \log_{10} e.$$

Having determined the concentrations for the calculated Stokes diameters, frequencies undersize are determined using equations (9), (10) and (11).

For the centrifuge dimensions and fill volume stipulated in (a) and (b), F and y can be calculated as follows.

(a) Centrifuge dimensions

R_0 (internal radius of centrifuge bowl) = 8.00 cm

h (internal thickness of centrifuge bowl) = 0.70 cm

R (radius to measurement zone) = 7.00 cm

(b) Fill volume. For a fill volume of 100.0 cm³

$$\pi(R_0^2 - S^2)h = 100.0$$

$S = 4.304$ cm (where S is the initial radius of the surface of the suspension, see 4.1)

(c) Calculation of y values

$$y = \left(\frac{R}{S} \right)^2 = \left(\frac{7.00}{4.304} \right)^2 = 2.645$$

For times in a 2:1 progression, $\frac{d_i}{d_j} = \frac{1}{\sqrt{2}}$ hence, from equation (8) the $y_{i,j}$ values can be calculated as follows:

$$\begin{aligned} y &= 2.645 \\ y_{1,2} &= 1.626 = y_{2,3} = y_{3,4} = y_{4,5} = y_{5,6} = y_{6,7} = y^{1/2} \\ y_{1,3} &= 1.275 = y_{2,4} = y_{3,5} = y_{4,6} = y_{5,7} = y^{1/4} \\ y_{1,4} &= 1.129 = y_{2,5} = y_{3,6} = y_{4,7} = y^{1/8} \\ y_{1,5} &= 1.063 = y_{2,6} = y_{3,7} = y^{1/16} \\ y_{1,6} &= 1.031 = y_{2,7} = y^{1/32} \\ y_{1,7} &= 1.015 = y^{1/64} \end{aligned}$$

(d) Calculations of F values

$$\text{From equation (11) } F_1 = (1/2) (1 + 2.645) C_1, F_1 = 1.823 C_1$$

From equation (9) for $j = 1, i = 2$

$$\begin{aligned} F_2 &= (1/2) (2.645 + 1.626) C_2 + \\ &+ \left(\frac{2.645 + 1.626}{2.645 + 1.626} - \frac{2.645 + 1.626}{1.626 + 1} \right) F_1 \\ &= 2.136 C_2 - 0.626 F_1 \\ &= 2.136 C_2 - 1.142 C_1 \end{aligned}$$

Continuing in a like manner gives the full solution (see table 1).

Table 1. F values for X-ray centrifuge

$$\begin{aligned}
 F_1 &= 1.823C_1 \\
 F_2 &= 2.136C_2 - 1.142C_1 \\
 F_3 &= 2.136C_3 - 1.008C_2 - 0.200C_1 \\
 F_4 &= 2.136C_4 - 1.008C_3 - 0.174C_2 + 0.023C_1 \\
 F_5 &= 2.136C_5 - 1.008C_4 - 0.174C_3 + 0.021C_2 + 0.024C_1 \\
 F_6 &= 2.136C_6 - 1.008C_5 - 0.174C_4 + 0.021C_3 + 0.021C_2 + 0.006C_1 \\
 F_7 &= 2.136C_7 - 1.008C_6 - 0.174C_5 + 0.021C_4 + 0.021C_3 + 0.005C_2
 \end{aligned}$$

15 Tests in duplicate

See clause 8.

16 Report

See clause 9.

17 Worked example

Material	Iron oxide
Temperature	24 °C
Dispersant	0.1 % (m/m) sodium polymetaphosphate in water
Viscosity, η	0.001 N·s/m ²
Powder density, σ	5130 kg/m ³
Liquid density, ρ	1000 kg/m ³
Initial concentration	0.87 g in 100 cm ³
Full scale deflection	96 divisions
Scale expansion	(× 3) hence $L_0 = 288$ divisions
Centrifuge speed, N	750 r/min
ω	25 π rad/s

$$d_1 = \sqrt{\left(\frac{18 \times 0.001 \times \ln \frac{7.00}{4.304}}{4130 \times (25\pi)^2 \times 60} \right)} \quad (\text{see equation (3)})$$

$$d_1 = 2.39 \mu\text{m}$$

The example is tabulated in table 2.

Table 2. X-ray centrifuge analysis

T	Deflection (divisions)			C	$d^\dagger$	F
	L	$(L_0 - L)$	$B'C^*$			
min				%	μm	%
0	57.5	230.5	967	100		
1	55.5	232.3	933	96.5	2.39	100
2	54.0	234.0	902	93.3	1.69	99.7
4	51.2	236.8	850	87.9	1.20	99.4
8	46.0	242.0	756	78.2	0.85	97.2
16	37.5	250.5	606	62.7	0.60	88.4
32	25.5	262.5	403	41.7	0.42	65.5
64	13.5	274.5	209	21.6	0.30	34.5
128	6.8	281.2	104	10.8	0.21	19.1
		extrapolated value		3.5	0.15	6.4

*See equation (19).
†See equation (2).

Section three. The pipette centrifuge method

18 Principle

The pipette centrifuge is essentially a centrifugal version of the fixed position gravitational pipette. With this instrument concentration changes are monitored at a fixed radius (R) by means of a sample extraction system. Particle sizes and concentrations undersize are determined using modified forms of equations (2) and (6).

19 Apparatus

The instrument (see figure 2) consists of a shallow bowl stainless steel disc (3) of internal radius 8 cm and depth 1.02 cm. Samples are extracted from a radius of 7 cm through six equally spaced narrow bore stainless needles (8) all connected by a hollow shaft. The samples are sucked into a 10 cm³ pipette (9) which may be filled precisely so that no excess liquid is extracted.

The centrifuge disc is driven at speeds of 750 r/min or 1500 r/min by an electric constant speed motor (5). A fan is incorporated in the motor housing to maintain temperature conditions constant during an analysis.

The disc (3) can be cleaned by removing the disc top (4) which is held by eight screws and sealed with a rubber 'O' ring (7).

20 Preparation

20.1 Analysis sample

Make up an analysis sample (usually 170 cm³) as described in 7.3 to give an initial concentration of about 0.2 % by volume. Then extract 2 × 10 cm³, using a pipette, for drying and weighing separately, as a double check for the 100 % concentration level. This sample should be dried at the same time, and under the same conditions, as the measurement samples since the mass loss of dispersing agents depends on the drying conditions. It is also advisable to dry a sample (say 25 cm³) of dispersing solution in order to determine whether the dried mass remains constant.

20.2 Temperature

Determine and record the temperature of the suspension; also record the liquid viscosity (determined directly or read off tables).

21 Procedure

Switch on the centrifuge at a suitable speed. (Usually 750 r/min unless the powder is known to be very fine.)

Pour the well-dispersed suspension into the centrifuge through the centre opening, as quickly as possible (5 s) and immediately start the clock.

Slide the sampling head (well greased) on to the rotating shaft, close the stopcock and apply moderate vacuum.

Extract exactly 10 cm³ of suspension. This will usually require opening the cock 10 s before the extraction time and closing it about 10 s after.

NOTE. Operators are recommended to familiarize themselves with the instrument by first carrying out a dummy run with clear dispersing liquid.

With very viscous liquids 20 s extraction time may prove insufficient; in these cases it has to be increased. If air bubbles are drawn in through the stopcock some grease should be applied to it.

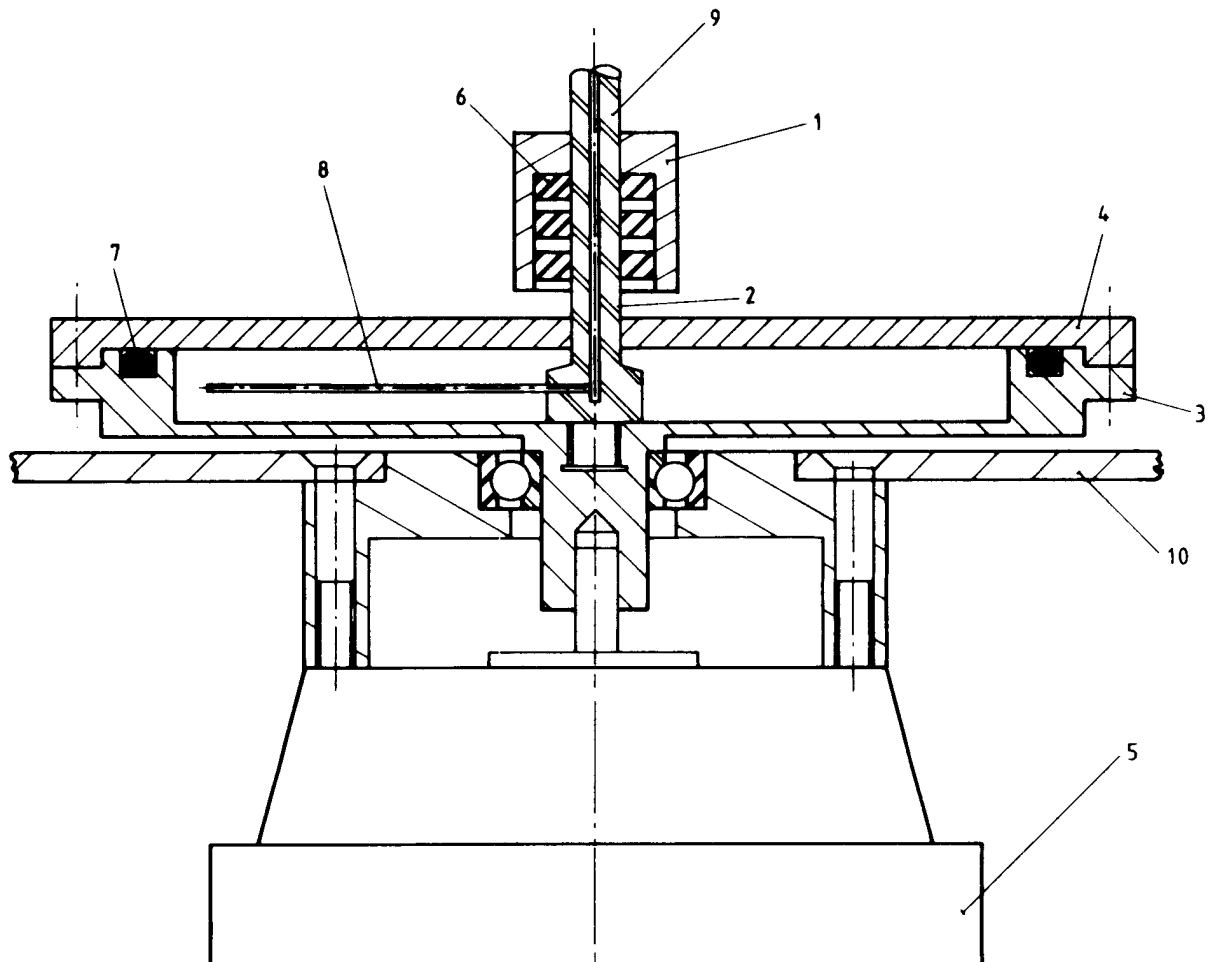
Close the cock, detach the vacuum and empty the pipette into a pre-weighed container, applying gentle pressure. Through the same outlet, suck in about 5 cm³ clear dispersing liquid (*not* solution), continue the suction to draw air into the pipette and then discharge into the same tared container. This cleans out the pipette in preparation for the next withdrawal.

Repeat this procedure at 2, 4, 8, 16 up to 64 or perhaps 128 min depending on the fineness of the powder. The analysis may be terminated if the extracted samples come out relatively clear. After the 4 min extraction, remove and re-attach the sampling head after and prior to each analysis respectively, in order to prevent overheating of the seals. The first sample may be extracted at any time provided subsequent times are in two-to-one progression. Stop the centrifuge and thoroughly clean by removing the lid.

Sample concentrations are usually determined by drying in an oven and weighing the containers to an accuracy of 0.1 mg, allowance being made for the presence of wetting agent by drying a sample of solution together with the extracted samples.

With powders or dispersing agents that are hygroscopic it is necessary to place the containers to cool in a desiccator after removing them from the oven. Weighing should be carried out rapidly to minimize errors.

The sample concentration of the final extraction should not exceed 5 % of the original concentration otherwise over-estimation of the percentage of 'fines' will occur. If this is not attained then a modest degree of extrapolation is permitted. Where this is not possible it is advisable to re-analyse at a higher centrifuge speed and a greater initial withdrawal time. Even with final concentrations well in excess of 10 % the coarse end of the distribution is determinable since the error in F due to this decreases with increasing d values (see clause 24).



- | | |
|-----------------------|--------------------|
| 1 Rubber seal housing | 6 Rubber seals |
| 2 Sampling head | 7 'O' ring |
| 3 Disc | 8 Needles |
| 4 Disc top | 9 Pipette |
| 5 Electric motor | 10 Centrifuge body |

Figure 2. The pipette centrifuge

22 Calculation of results

22.1 Calculation of limiting Stokes diameter

The largest particle present in the initial sample withdrawn at time t_1 when the measurement radius is R and the surface is at radius S , is given by equation (2) which may be written in the form:

$$d_1^2 t_1 = A \ln (R/S) \quad (20)$$

The largest particle present in the sample withdrawn at time t_r is:

$$d_r^2 t_r = A \ln (R/S) \left(1 + \frac{\Delta x_{1,r}}{x_{1,r}} \right)^{-1} \times \left(1 + \frac{\Delta x_{2,r}}{x_{2,r}} \right)^{-1} \dots \left(1 + \frac{\Delta x_{r-1,r}}{x_{r-1,r}} \right)^{-1} \quad (21)$$

The time for the second withdrawal is t_2 . The largest particle present in the withdrawn sample will have fallen from S to $x_{1,2}$ in time t_1 , then a further distance $\Delta x_{1,2}$ due to the withdrawal of the first sample.

In time t_3 particles of size d_3 will fall from the surface at radius S to $x_{1,3}$, then a further distance $\Delta x_{1,3}$ due to the withdrawal of the first sample. In the next time increment $(t_2 - t_1)$ the particles of size d_3 will fall from $(x_{1,3} + \Delta x_{1,3})$ to radius $x_{2,3}$ then a further distance $\Delta x_{2,3}$ due to the withdrawal of the second sample.

The terms in x in the equation (21) are, therefore, the correction terms for the fall in level at each extraction.

22.2 Calculation of cumulative percentage undersize

Calculate the concentration of particles in the suspension from the masses W_n of the fractions:

$$C = \frac{W_n}{W_0} \times 100 \quad (22)$$

where

W_n is the mass of fraction;

W_0 is the average mass of fraction withdrawn at $t = 0$ (see 20.1).

Denoting the lowest concentration, i.e. extraction at the maximum time, as C_1 which applies at d_n the smallest size, subsequent concentrations are C_2, C_3 and so on at sizes d_{n-1}, d_{n-2} and so on. The cumulative percentage undersize is then given by F_1, F_2 and so on using table 3.

Table 3. F values for pipette centrifuge in terms of experimental C values

$$\begin{aligned} F_1 &= 1.182C_1 \\ F_2 &= 1.311C_2 - 0.275C_1 \\ F_3 &= 1.412C_3 - 0.355C_2 - 0.053C_1 \\ F_4 &= 1.536C_4 - 0.479C_3 - 0.054C_2 - 0.004C_1 \\ F_5 &= 1.692C_5 - 0.646C_4 - 0.049C_3 + 0.002C_2 + 0.001C_1 \\ F_6 &= 1.893C_6 - 0.881C_5 - 0.028C_4 - 0.012C_3 + 0.003C_2 \\ F_7 &= 2.168C_7 - 1.218C_6 + 0.019C_5 + 0.028C_4 + 0.004C_3 \end{aligned}$$

NOTE 1. These values apply only for centrifuges with dimensions as given in clause 19 and are for an initial feed volume of 150 cm³ and seven extractions in a 2:1 progression in time.

NOTE 2. These F values hold for seven extractions only. If the concentration, C , falls to zero before seven samples have been extracted (say $C_2 = 0$) it is necessary to put $F_1 = F_2 = 0$ and $F_3 = 1.412C_3$ and so on.

It is recommended that not more than six extractions be made since by then, the radius of the internal surface of the suspension is 5.99 cm compared with a measurement radius of 7.0 cm. A height of fall of less than 1.0 cm may lead to unacceptable experimental errors.

23 Evaluation of results

A plot of concentration (as a percentage of the initial concentration) against time should be made to check any deviations due to possible experimental errors. In order to space out the unequal time intervals the use of log-probability paper is recommended for this purpose, alternatively a plot of concentration against the square root of time is acceptable.