
British Standard Methods for

Determination of particle size distribution

Part 2. Recommendations for gravitational liquid sedimentation methods for powders and suspensions

Méthodes de détermination de la granulométrie

Partie 2. Méthodes de sédimentation par liquide de gravitation pour poudres et suspensions — Recommandations

Verfahren zur Bestimmung der Korngröße

Teil 2. Empfehlungen für Verfahren zur Sedimentation im Schwerefeld für Pulvern und Suspensionen

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Methods for determination of particle
size distribution
Part 2. Recommendations for gravitational liquid
sedimentation methods for powders and
suspensions

Correction

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November 1984

Clause 4.3 Lower size limit
In paragraph 2, line 5, delete '0.5 m/s' and substitute '0.5 $\mu\text{m/s}$ '.

Foreword

This British Standard, prepared under the direction of the Chemical and Petroleum Engineering Standards Committee, supersedes BS 3406 : Part 2 : 1963 which is withdrawn.

This revision 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 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 methods
- Part 5 Recommendations for electrical sensing zone method (the Coulter principle)
- Part 6* Recommendations for centrifugal liquid sedimentation methods for powders and suspensions

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, to facilitate comparisons of size analyses made in different laboratories.

Several methods of size analysis are recommended because of the varying properties of the powders and the differing circumstances of usage. The conditions of test should correspond with the conditions of use. A powder used in a wet process should be tested in a wetted state. A dry powder may be tested by liquid sedimentation or other methods but if used in an air dispersed condition it may be better to analyse it by air elutriation. Such co-ordination is not always necessary or possible, but samples that are collected in the wet state should not be dried before analysis unless it can be proved that all aggregates formed on drying will be dispersed completely without any attrition of the particles.

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, density, solubility, refractive index;
- (c) aggregation and dispersion characteristics of the powder;

- (d) the amount of material available for analysis;
- (e) the method by which the gross sample has been collected;
- (f) the conditions under 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 (see appendix D). 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. Standardization between laboratories is best established by the use of certified reference materials for example those of the Community Bureau of Reference (BCR) referred to in appendix C.

The electrical sensing zone method is a widely used method of particle size analysis as large numbers of particles can be counted and sized at high speed with a good degree of accuracy. The external volume of each particle is measured independently of the density and refractive index of the particle. Response is affected only to a small extent by the shape and the resistivity of the particle, and these effects can be minimized by calibration. The limitation to the method is that the particles have to be suspended in an electrically conducting solution, or electrolyte.

Since the size-dependent properties measured are different for the various techniques, the resulting size analysis made on identical powders will also differ, the divergence increasing with increasing irregularity of particle shape. It is therefore essential when reporting an analysis that the method used be named.

Good reproducibility does not necessarily imply accuracy.

BS 410 specifies sieves for testing the size distribution of granular products in the particle size range from 125 mm to 38 µm and ISO 3310 'Test sieves — Technical requirements and testing', published by the International Organization for Standardization, specifies sieve sizes down to 20 µm.

The use of centrifuges for the analysis of particles less than about 5 µm in size by centrifugal sedimentation will be covered in BS 3406 : Part 6.

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

*In course of preparation.

British Standard Methods for

Determination of particle size distribution

Part 2. Recommendations for gravitational liquid sedimentation methods for powders and suspensions

1. Scope

This Part of BS 3406 describes the following liquid sedimentation methods for determining the particle size distribution of powders and suspensions and methods for obtaining a good dispersion in the suspension.

(a) *Incremental methods*

(1) Pipette methods:

- (i) fixed position pipette (Andreasen);
- (ii) variable position pipette.

(2) Absorption of electromagnetic radiation methods:

- (i) photosedimentation;
- (ii) X-ray sedimentation.

(b) *Cumulative methods*

- (1) Type 1. Sedimentation balance.
- (2) Type 2. Sedimentation balance.

NOTE. The titles of the publications referred to in this standard are listed on the inside back cover.

2. Definitions

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

2.1 gross sample. The final sample obtained or prepared from the bulk material under the sampling plan from which possible sub-division for testing, reference or storage can be made.

2.2 laboratory sample. The sample delivered to the laboratory. This may be the gross sample. Alternatively the laboratory sample may or may not be representative of the gross sample depending on the procedure used to obtain it (see BS 3406 : Part 1).

2.3 spot sample. A sample of specified quantity taken from a specified place in the bulk material, gross sample or laboratory sample, or at a specified place and time in a stream, and representative of its own local environment.

2.4 test sample. The sample prepared from the laboratory sample from which the test portions are withdrawn.

2.5 test portion. That portion withdrawn from the test sample and entirely used in the test or observation.

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

Section one. General

3. Principles

3.1 General. Sedimentation methods are based on the measurement of the rate of settling of the powder particles dispersed in a fluid, and are classified as either incremental or cumulative (see figure 1). In both classifications the powder may be introduced either as a thin layer on top of a column of fluid, the line start technique; or uniformly dispersed in the fluid, the homogeneous suspension technique. The latter is the one more often used in gravitational sedimentation and described here, whereas the former is more applicable to centrifugal sedimentation and is described in detail in BS 3406 : Part 6*.

3.2 Incremental methods. The fixed position pipette method gives the mass distribution directly, but the flexibility of the variable position pipette may be preferred for some routine applications. The photosedimentation technique is suitable when many routine comparisons need to be carried out but does suffer defects when used as an absolute method. The X-ray sedimentation technique is suitable for quantity routine size determinations of X-ray opaque powders (atomic number $M > 13$).

In incremental methods the solids concentration at the measurement level determines directly the proportion by mass of the analysis sample that consists of particles having a diameter less than that corresponding to the velocity of fall at the time of sampling. At zero time the concentration is taken as the 100 % value; at a later time the relative concentration (as compared with the zero time concentration) is equal to the cumulative mass fraction smaller than the Stokes diameter. The analysis can be terminated at any time therefore, to give the mass distribution curve for particles larger than the Stokes diameter at the experimental point at termination. Incremental methods are preferable for measuring wide size distributions completely as the smallest particles present have to settle the full settling height.

3.3 Cumulative methods. Cumulative sedimentation is used with sedimentation balances and may be preferred when a mass distribution is required directly and only a small amount (about 0.5 g) of powder is available. Two types of sedimentation balance are recommended for a size range of about 75 μm to 1 μm although it may be possible to extend the range if special criteria are met.

*In course of preparation.

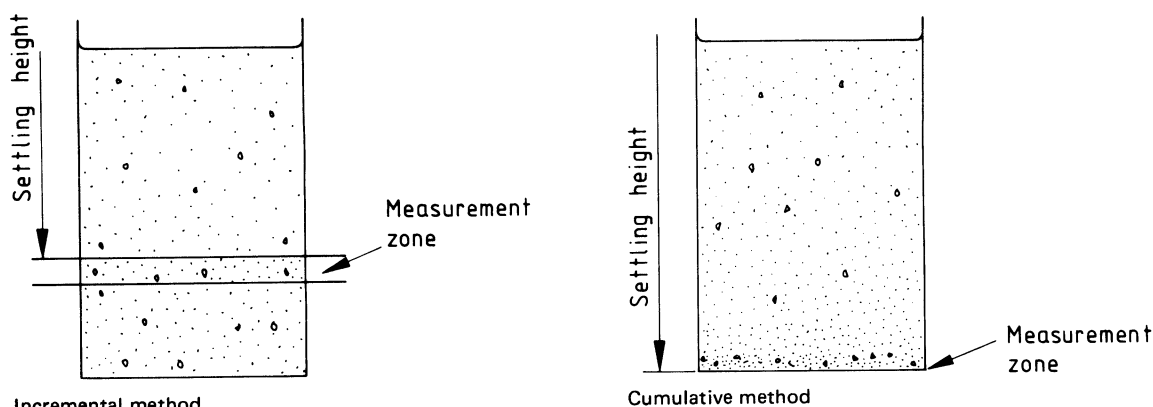


Figure 1. Methods

4. Calculation

4.1 Calculation of particle size. The calculation of particle size is dependent on Stokes' law which may conveniently be stated in the following form:

$$d_{St} = \left(\frac{18\eta h}{(\sigma - \rho)gt} \right)^{1/2} \quad (1)$$

where

d_{St} is the Stokes diameter, defined as the diameter of a sphere which has the same density and the same free falling velocity in a given fluid as the particle within the viscous flow region;

η is the absolute viscosity of fluid;

σ is the apparent density of particle*;

ρ is the density of fluid;

h is the distance through which particle falls in time t ;

$h/t (= v)$ is the free falling velocity;

g is the acceleration due to gravity.

4.2 Upper size limit. Stokes equation is valid only in the region of viscous (or laminar) flow, which sets an upper limit to the size of particle to be tested by this means. The limit is determined by the magnitude of the Reynolds number, a dimensionless quantity defined by:

$$Re = \frac{\rho v d_{St}}{\eta} \quad (2)$$

The Reynolds number should not exceed 0.25 if the error in Stokes diameter is not to exceed 3 %. As the Reynolds number increases laminar flow conditions no longer prevail and the turbulence set up behind a sedimenting particle causes it to settle more slowly than predicted by Stokes equation. If the particles are approximately spherical the true diameter may be determined using a known unique relationship between drag coefficient C_D , as defined in BS 2955, and Reynolds number [1] †.

Putting $Re = 0.25$ and equating equations (1) and (2) gives, for the limiting Stokes diameter d_{Stc} .

$$d_{Stc} = \left[\frac{4.5 \eta^2}{(\sigma - \rho) \rho g} \right]^{1/3} \quad (3)$$

For example, for silica $\sigma = 2650 \text{ kg/m}^3$, sedimenting in water, $\eta = 0.001 \text{ N s/m}^2$, $\rho = 1000 \text{ kg/m}^3$, $d_{Stc} = 65.3 \text{ } \mu\text{m}$.

At low Reynolds number the orientation of non-spherical particles is random hence a single particle will have a range of settling velocities. As the Reynolds number increases, particles tend to orientate themselves to give maximum drag and will settle at the slowest of the range of velocities possible with random orientation [2].

The time required for a particle to reach its steady (terminal) velocity is negligible but excessively short sedimentation times should be avoided. The maximum velocity should not exceed 0.3 cm/s. Concentration measurements fluctuate, due to the initial agitation, up to a time of about 1 min.

4.3 Lower size limit. For incremental methods, in any extracted sample, a range of maximum Stokes diameters exists depending on the range of settling heights in the increment. This affects the ability to define the distribution curve.

NOTE. Heywood [3] considers that the resolution, as defined by height of measurement zone divided by settling height, should be less than 1/7.

The lower size limit is due in part to the long sedimentation times, or high resolutions, required for fine particles. For example, a $1 \text{ } \mu\text{m}$ particle settling under gravity, with $(\sigma - \rho)$ of 1000 kg/m^3 and $\eta = 0.001 \text{ N s/m}^2$ (water), has a settling velocity of about 0.5 m/s. For a settling distance of 10 cm, 51 h are required. For a height of measurement zone of 1 mm, readings should not be taken nearer to the surface than 7 mm, leading to a settling time of 3.57 h.

In addition convection currents tend to build up during a protracted analysis. These may arise owing to temperature variations caused by uneven heating or cooling of the suspension. Temperature control requirements increase with increasing fineness of powder. Particle concentration variations within the suspension also occur; these have been attributed to the walls of the sedimentation vessel (or elements within the walls, e.g. stirrer) being slightly out of vertical; an alternative explanation is based on the inherent instability of sedimenting suspensions by which return flow of displaced liquid tends to be along vertically inclined surfaces [4].

Brownian motion gives a spread of settled positions for particles of the same size originating from the same initial position. For example, the $1 \text{ } \mu\text{m}$ particle discussed in

*Equal to the true density of non-porous particles only.

†The numbers in square brackets used throughout the text of this standard refer to the bibliographic references given in appendix E.

paragraph two of 4.3 has a root mean square displacement due to Brownian motion of 0.75 m/s which exceeds the settling velocity.

For these reasons sedimentation under gravity is recommended only down to a Stokes diameter of about 2 µm to 3 µm depending on the settling times involved.

4.4 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 finite distances and mutually affect each other and are also affected by neighbouring surfaces. In order to reduce these effects as far as possible, small concentrations should be used. A recommended upper volume concentration is 0.2 % and the distance between vertical 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 if the concentration effects are negligible.

5. Suspension and dispersion

5.1 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.

- (a) The solid should not dissolve or change chemically in the liquid and should also not swell or contract.
- (b) The liquid should inhibit the formation of agglomerates during sedimentation. This may often only be achieved by the addition of wetting or dispersing agents. (See appendix A.)
- (c) It is essential that the density of the liquid is less than the density of the solid. If the difference between the density of the particles and the density of the liquid is less than 500 kg/m³, it is essential that special care is taken to avoid convection currents.
- (d) It is essential that the viscosity of the liquid is selected so that, on the one hand, the analysis does not take too long and, on the other hand, the coarsest particles do not settle too rapidly.

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 5.2 to 5.4. After selection of a suspending system the suspension is prepared according to 5.4 and its state of dispersion assessed in accordance with 5.3.

5.2 Tests for dispersion

5.2.1 Microscopical examination. This test should always be carried out. A small drop of the suspension is 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. Unless extreme care is taken with suspensions in mobile liquids, lowering of the cover slip on to the suspension

will cause preferential removal of the larger particles to the edge of the cover slip. As these particles may have smaller particles attached to them, a false idea would then be given of the degree of dispersion.

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

5.2.2 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 standing. 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. The appearance of the sediment itself is also a guide, as a good dispersion will yield a rigid sediment of minimum volume, while a flocculated suspension will produce a relatively large volume of sediment which will move like a liquid on tilting the tube. In a tilted tube a flocculated dispersion will also give a visible deposit on the wall.

5.2.3 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.

5.3 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.

These tests require a good deal of time and are only recommended when it is intended to carry out major test series with similar systems.

5.4 Preparation for a sedimentation analysis. A suspending liquid should be selected, (see appendix A). If not already known, determine the viscosity of the liquid at the measuring temperature. It is essential that the viscosity of the liquid is such that the Reynolds number characterizing the flow round the largest particles of the powder is not greater than 0.25.

If not already known, determine the density of the liquid at the measuring temperature and the density of the particles in accordance with BS 733. The amount of material available is generally greater than the amount needed for the analysis. A representative analysis sample should therefore be obtained from the laboratory sample (see BS 3406 : Part 1). The whole of the analysis sample should be used in the subsequent analysis.

As indicated in 4.2, the settling velocity of the largest particles of the analysis sample is not permitted to exceed a certain value. If the size distribution of particles smaller than this size is required the whole of the analysis sample can be used and the time of the first withdrawal selected to give this value. For incremental and some cumulative

methods, the 100 % value may be calculated from the mass of sample used. The size distribution of the oversize fraction can be found by repeating the analysis using a more viscous liquid so that the coarsest particle present in the sample is less than that given by the limiting Reynolds number.

Alternatively, remove oversize particles, for example, by wet or dry sieving (see BS 1796). Wet sieving should be carried out with the liquid later to be used as the sedimentation liquid and the total quantity of liquid used should not exceed the capacity of the sedimentation vessel. Otherwise, use a representative portion of this suspension for the sedimentation analysis. Record the percentage residue on the sieve. If this is substantial it is necessary to carry out a sieve analysis and combine the two sets of data. The data from this sieve analysis carried out on a further withdrawn portion of the laboratory sample should be combined with the sedimentation data. See appendix B.

At the stage at which the analysis sample is to be wetted, slowly add the dispersing solution or liquid, work to a paste and then a liquid suspension with a suitable instrument 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.

Place the sedimentation vessel in a water bath, thermostat or room at constant temperature (± 1 K) in a vertical and stable position, free from vibration. If the vessel is not absolutely vertical density currents are set up which give rise to errors of measurement of very small particles. It is essential that the rate of change of temperature is kept less than ± 0.01 K/min for prolonged analyses (greater than 1 h). This can be achieved in sufficiently large water baths and careful setting of the thermostat to give heating and cooling periods as long as possible. If the temperature of the sedimentation vessel and its contents is not the same as the temperature of the water bath, leave the vessel in the water bath for a time sufficiently long for temperature equilibrium to be achieved. For example, a 40 mm diameter vessel containing 500 cm³ of liquid will take approximately 4 h to equilibrate at 10 K above its original temperature. Any possibility of heating on one side, e.g. by radiation from a heat source, is to be avoided.

If evaporation of the sedimentation liquid occurs, the upper layer of liquid cools and this gives rise to convection currents. The sedimentation vessel should therefore be sealed as closely as possible.

6. Tests in duplicate

Carry out tests in duplicate on representative analysis samples 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 %.

7. Report

Plot the results of the analysis with the Stokes diameter as abscissae and the percentages undersize as ordinates. Select from the smooth curve drawn through the points cumulative 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 fixed position pipette (Andreasen) method

8. Principle

Samples are withdrawn from the suspension during sedimentation by means of a calibrated pipette at a series of known times after initial agitation, the tip of the pipette being at a known depth, h , below the surface. After time t , the sample withdrawn contains only those particles with Stokes diameters less than that of particles settling at rate h/t , since all particles larger than this will have settled below the sampling point. The cumulative undersize distribution by mass of the powder is obtained directly by weighing the residue after removal of the suspending medium from the sample.

9. Apparatus (see figure 2)

9.1 Sedimentation vessel, consisting of a glass sedimentation vessel of about 5 cm internal diameter having a graduated scale 0 cm to 20 cm, marked on the side of the vessel, which may be subdivided at 5 mm or 10 mm intervals. The zero graduation should be not less than 25 mm from the inside base of the vessel so that the capacity, when filled to the 20 cm mark is about 450 cm³. It is important that the walls of the cylinder are vertical. The scale should also be vertical and have an accuracy of ± 1 mm.

9.2 Pipette, fitted with a two way tap and a side discharge tube. The capacity of the pipette to the graduation mark is 10 cm³. A bell-shaped dome is fused to the pipette with a ground-glass joint to fit the neck of the sedimentation vessel. A small vent hole is made in this dome. The pipette bulb should be olive-shaped. The inlet to the pipette stem should be level with the zero mark on the sedimentation vessel and the stem should be parallel to the walls of the sedimentation vessel when in position. The stem from the pipette bulb to the sampling inlet is constructed of capillary glass tube with a bore not less than 1 mm nor more than 1.3 mm. The tube above the bulb should be 3.5 mm bore.

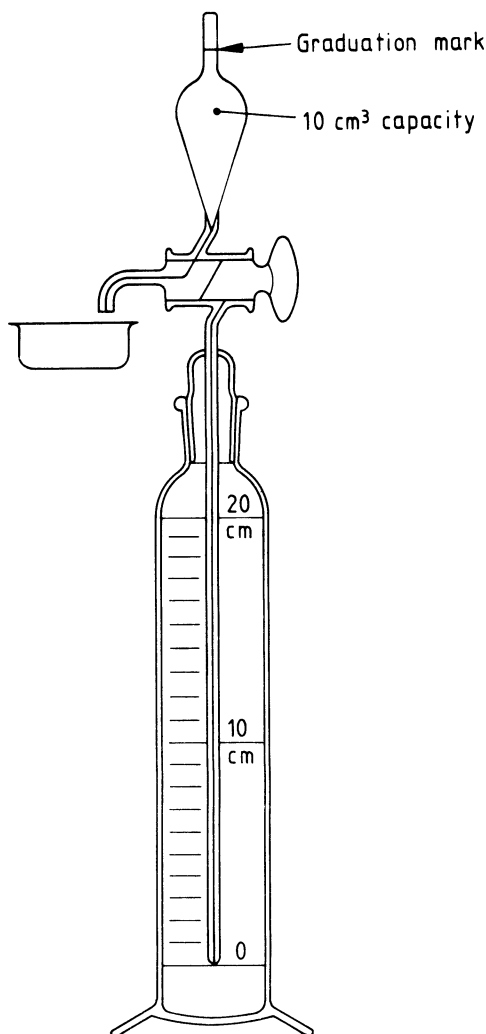


Figure 2. Fixed position pipette

10. Ancillary apparatus

10.1 Constant temperature enclosure. For prolonged analyses (greater than 1 h) a constant temperature bath of at least 15 L capacity, into which the sedimentation vessel can be immersed up to the graduation mark is required. It is essential that no vibration be imparted to the sedimentation vessel during the analysis.

10.2 Dispersing vessel of appropriate dimensions.

10.3 Flexible spatula.

10.4 Ultrasonic bath, bottle shaker or high speed mechanical stirrer rotating at a suitable speed (500 r/min to 1000 r/min).

10.5 Balance having a sensitivity of not less than 0.1 mg.

10.6 Drying oven capable of being maintained within the temperature range suitable for the evaporation of the suspending liquid, e.g. 105 °C to 110 °C for water.

10.7 Wide mouthed weighing bottles, suitable for evaporation, of capacity not less than 20 cm³ or **aluminium foil containers.** Aluminium foil containers, as purchased, may contain a layer of grease and should be oven dried before use. These are preferable to glass containers since they weigh only about 1 g as opposed to 20 g to 30 g and, since a difference mass is required, greater accuracy results from their use. With certain systems a filtration system may be preferred.

10.8 Desiccator in which the sample containers can be cooled after drying.

10.9 Timer.

11. Preparation

11.1 Calibration of sedimentation vessel. Determine the volume (V) of the sedimentation vessel, to an accuracy of 0.3 %, by filling with distilled water up to the 20 cm mark with the pipette in position. Remove eight 10 cm³ samples and determine the final height of suspension, hence determine the change in height (Δh) after each withdrawal.

11.2 Calibration of pipette. Clean and dry the pipette. Partly fill the sedimentation vessel with distilled water. Set the tap in the sampling position and suck water into the bulb to the level of the graduation mark. Reverse the tap to the discharge position and allow the water to drain into a tared weighing container. Apply pressure to blow any water remaining in the bulb and the discharge tube into the weighing container. Weigh the bottle to the nearest 0.001 g and calculate the internal volume V_p , of the pipette.

11.3 Temperature. Maintain the temperature in accordance with 5.4.

11.4 Analysis sample. Make up the analysis sample as described in section one to give a concentration of about 0.2 % by volume.

11.5 Withdrawal time calculation. Calculate the withdrawal time for the first fraction using Stokes law in the following form:

$$t_1 = \frac{18\eta h}{(\sigma - \rho)gd_1^2} \quad (4)$$

with $t_1 \geq 60$ s and

where d_1 is the limiting Stokes diameter for the first fraction and does not exceed the critical Stokes diameter as given by equation (3).

The initial height h is normally 20 cm but other heights in the 10 cm to 20 cm range may be used.

Extract at times calculated from selected diameters, or alternatively at times in a ratio of two to one commencing at, say, 1 min.

If the coarse end of the size spectrum is required ($> d_{Stc}$), a repeat analysis, using a higher viscosity liquid, needs to be carried out and continued until there is sufficient overlap between the two determined distributions.

12. Procedure

Transfer the suspension without loss to the sedimentation vessel. With the pipette in position, fill to the 20 cm mark using the suspending liquid. Transfer to the constant temperature enclosure/bath and allow to stand until temperature equilibrium has been attained. Record this temperature, which should not differ greatly from that of the room. When temperature equilibrium has been attained mix the contents thoroughly by placing a finger over the vent hole in the dome and inverting continuously for 1 min.

Use the following technique for extracting samples.

The time to fill the pipette should be about 20 s; commence extraction 10 s before the withdrawal time and terminate 10 s after. Discharge the fraction into a

tared weighing container. When the pipette bulb has drained, draw 5 cm³ to 7 cm³ of suspending liquid without dispersant from a container into the bulb through the outlet tap. Then remove the container but maintain a slight vacuum in order to draw air into the pipette bulb; then apply pressure and wash the liquid into the tared weighing container. This removes any particles adhering to the surface. Keep the stem of the pipette full of suspension.

Withdraw a sample immediately following the inverting process, repeat the inverting process and withdraw a further sample. If these two masses do not agree to within 2 %, reject the analysis. The average of these two masses constitutes the 100 % mass. Repeat mixing; clamp the sedimentation vessel in position, simultaneously starting the timer. Withdraw fractions at time intervals as explained in 11.5.

The depth of immersion of the pipette decreases as each fraction is withdrawn. Determine the exact decrease in depth by experiment, and allow for it in the subsequent calculations. Suppose that the decrease is 0.4 cm for each fraction withdrawn, and that at time zero the depth of immersion of the pipette was 19.2 cm, then the depth after the first timed fraction has been withdrawn will be 18.8 cm, and the mean depth used for calculation of the initial diameter will be 19.0 cm. The mean depth for the second fraction will be 18.6 cm, and so on.

13. Assay of fractions

13.1 Procedure. Accurately assay each fraction; if by drying and weighing adopt the following procedure:

Evaporate each fraction in its weighing container to dryness in an oven maintained at a temperature suitable to the particular suspending liquid and cool in a desiccator. Appropriate precautions should be taken if hazardous liquids are used. Weigh the weighing container and contents to the nearest 0.1 mg and determine the mass W_n of solid material in each of the fractions ($n = 1, 2, \dots$). Make allowance for the mass of dispersing agent retained after evaporation. This allowance is best made by drying a 20 cm³ sample of suspending liquid plus dispersant with the withdrawn samples.

The removal of the suspending liquid may be expedited by first centrifuging the fractions collected in centrifuge tubes and decanting the supernatant liquid from the firmly compacted solid material. Then proceed as in the preceding paragraph.

Fractions may be assayed by other appropriate methods, e.g. chemical or colorimetric.

13.2 Calculation of Stokes diameters. If the times of sampling have been other than those recommended in 11.5, calculate the limiting Stokes diameters d_n corresponding to each of the time intervals t_n ($n = 1, 2, 3, \dots$).

$$d_n = \left(\frac{18h}{(\sigma - \rho)gt_n} \right)^{1/2} \quad (5)$$

13.3 Calculation of cumulative frequencies undersize.

Calculate the cumulative frequencies F_n by mass of particles smaller than each of the Stokes diameters d_n for each time interval t_n from the masses W_n of the fractions:

$$F_n = 100 \frac{W_n V}{W_s V_p} \quad (6)$$

where

W_n is the mass of fraction (in g);

W_s is the mass of test portion (in g);

V is the volume of sedimentation vessel to the initial mark (in cm³);

V_p is the volume of pipette (in cm³).

W_s/V should, within experimental limits, be equal to W_o/V_p where W_o is the 100 % mass.

If W_s/V and W_o/V_p do not agree to better than 5 % it is essential that repeat tests be carried out. If the disagreement persists the cause should be investigated.

14. Tests in duplicate

See clause 6.

15. Report

See clause 7.

NOTE. Leschonski modifications [5]. In the theory for the Andreasen method it is assumed that the sample is withdrawn from a narrow cylindrical element, whereas the actual sampling zone is to a first approximation a sphere. Leschonski showed that the error introduced is less than 1 % provided the ratio of sphere radius to sedimentation height remains below 0.1. Also with the vertically downward positioned pipette of the Andreasen apparatus there is a liquid volume below the tip of the pipette into which no solid particles can sediment from the layers above. This situation creates an instability which results in the setting up of density difference convection currents around the lower end of the pipette.

To overcome these errors Leschonski designed a pipette to conform with the theory. The pipette is extended to the bottom of the vessel and the sample withdrawn through a series of holes around its circumference at a fixed depth. Leschonski also showed that in the case of the Andreasen pipette the small amount of liquid retained in the capillary tube after each withdrawal gives rise to a systematic positive error, i.e. an overestimation of the percentage undersize. If this error is to be completely avoided the sample residue has to be removed from the capillary shortly before taking the next sample. To eliminate this error Leschonski suggested a pipette incorporating a subsidiary bulb with a volume matched to that of the capillary.

He therefore suggested that the pipette should consist of a capillary which extends to the bottom of the vessel with four withdrawal apertures, staggered by 90°, located about 30 mm above the bottom of the vessel. The shape of the bulb was to be unconventional with a gradual transition from bulb to stem to reduce the possibility of overrunning the upper fiduciary mark. He also suggested that the tap should be of PTFE so as to avoid particles adhering to the ground-glass assembly of the stopcock.

In practice, differences between results obtained using these modifications and results using the Andreasen pipette method are not significant.

16. Worked example (Andreasen pipette)

Sample	quartz
Medium	distilled water
Density of medium	999 kg/m ³
Density of powder	2650 kg/m ³
Temperature	20 °C
Viscosity of medium	0.001005 N·s/m ²
Dispersing agent	0.1 % (V/V) Na ₄ P ₂ O ₇ (sodium polyphosphate)
Sample mass	2.205 g
Volume of sedimentation vessel	455 cm ³
Volume of pipette	9.88 cm ³
Powder concentration	4.845 g/L = 0.18 % (V/V)

The example is tabulated in Table 1.

Table 1. Worked example (Andreasen pipette)

Container number	Withdrawal time	Drop height	Container mass	Container and residue mass	Residue mass	Mass of powder in residue	Stokes diameter	Cumulative mass undersize
1	Mass of Na ₄ P ₂ O ₇ in 10 cm ³		g	g	g	Average mass of Na ₄ P ₂ O ₇ in 9.88 cm ³ = 0.0083 g		
2			1.2383	1.2467	0.0084			
			1.2595	1.2680	0.0085			
3	min	cm				Average 100 % mass = (0.0563 – 0.0083) = 0.0480 g		
4	0		1.2379	1.2944	0.0565			
	0		1.1853	1.2414	0.0561			
5	2.27	17.74	1.1933	1.2497	0.0564	g	μm	%
6	4.40	17.18	1.2120	1.2682	0.0562	0.0481	38.1	100
7	8.51	16.62	1.1716	1.2277	0.0561	0.0479	27.0	99.8
8	16.45	16.05	1.1881	1.2405	0.0524	0.0478	19.1	99.6
9	31.74	15.49	1.2224	1.2637	0.0413	0.0441	13.5	91.9
10	61.18	14.92	1.2224	1.2637	0.0413	0.0330	9.53	68.8
11	117.71	14.36	1.1715	1.1937	0.0222	0.0139	6.74	29.0
12	227.03	13.80	1.2206	1.2343	0.0137	0.0054	4.77	11.3
13	433.80	13.23	1.1969	1.2086	0.0117	0.0034	3.36	7.1
			1.2350	1.2444	0.0094	0.0011	2.38	2.3

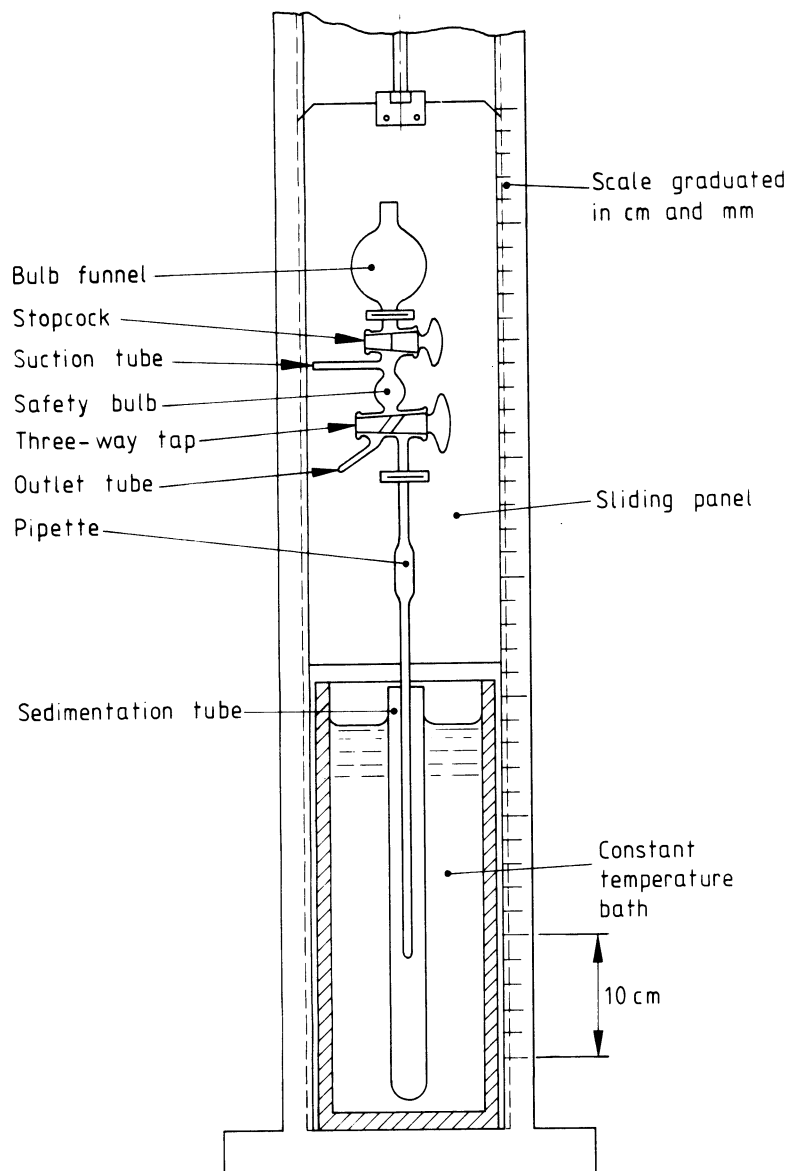


Figure 3. The variable position pipette

Section three. The variable position pipette method

17. Principle

See clause 8.

18. Apparatus (see figure 3)

18.1 Sedimentation tube, of glass, about 5 cm in diameter and approximately 35 cm long, graduated at a known volume (V) of the order of 500 cm^3 .

18.2 Pipette, of capacity 10 cm^3 with a pressure and suction inlet, arranged so that it can be inserted to a known depth in the sedimentation tube when the latter is immersed in a constant temperature bath.

18.3 Ancillary apparatus. See clause 10.

19. Preparation

19.1 Calibration of pipette. Clean and dry the pipette and rinse in distilled water. Close the stopcock, open the three-way tap and, using the suction tube, suck up distilled water into the pipette until it rises into the safety bulb. Close the tap and withdraw the pipette from the water. Allow the excess water, above the three way tap, to drain through the outlet tube. Discharge the water contained in the pipette and the three way tap into a tared weighing bottle and weigh to the nearest 0.001 g . Calculate from this mass the internal volume, V_p , of the pipette and the three-way tap.

Clean thoroughly the pipette, the sedimentation vessel and the dispersing vessel, rinse with distilled water and dry.

19.2 Temperature. Maintain the temperature in accordance with 5.4.