"Particle Size Distribution/Fibre Length and Diameter Distributions"

Method A: Particle Size Distribution (effective hydrodynamic radius)

Method B: Fibre Length and Diameter Distributions

1. INTRODUCTORY INFORMATION

• Prerequisites

Method A: – Water insolubility
Method B: – Information on fibrous nature of product
– Information on stability of fibre shape under electron-microscopic conditions

• Guidance information

Method A: – Melting point

Method B: – Melting point

• Qualifying statements

Both test methods can be applied to pure and commercial grade substances.

Method A:

This method can only be applied to water-insoluble ($< 10^6$ g/l), powdered type products.

The equivalence of the six national and international standard methods for particle size distribution was not tested, and is currently not known. There is a particular problem in relation to sedimentation and Coulter counter measurements.

Method B:

This method applies only for fibrous products. The effect of impurities on particle shape should be considered.

• Recommendations

Method A:

Equivalence of the methods for determination of particle size distribution should be tested in the laboratory.

• Standard documents

The "Effective Hydrodynamic Radius Determination" is based on the following standards:

– ASTM - D 3360, D 422
– NF-T 30044
– DIN - 66115
– DIN - 66116, Part 1
– ASTM - C 678
– ANSI - C 690 - 75

and on a test principle described in Chem. Ing. Tech. 46, 729 (1974).

2. METHOD

A. INTRODUCTION, PURPOSE, SCOPE, RELEVANCE, APPLICATION AND LIMITS OF TEST

Many methods are available for particle size measurements, but none of them is applicable to the entire size range. Sieving, microscopic sedimentation and elutriation techniques are most commonly employed. Moreover, in the case of airborne particles (dusts, smokes, fumes) radiation scattering and inertial methods prove particularly useful. Finally, appropriate sampling procedures should be selected in order to prepare specimens really representative of the material under test (Method A).

The first method described in this Guideline (Method A) is designed to provide information on the transportation and sedimentation of insoluble particles in water and air. In the special case of materials which can form fibres, an additional set of measurements (Method B) is also recommended to help identify potential health hazards arising from the inhalation or ingestion.

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Method A is generally applicable, frequent in use and hydrodynamic in character; Method B is comparatively specialised, infrequently required and involves microscopic examination. It should be borne in mind, however, that the original particle size distribution is highly dependent on the industrial processing methods used and can also be affected by subsequent environmental or human transformations.

These tests are applicable only to water insoluble (solubility < 10^6 g/1) substances. Method B for fibres will be applied only if light microscopic examination, similarities to known fibrous or fibre-releasing substances or other data indicate a likelihood that fibres are present. In this context, a fibre is a water insoluble particle, of aspect ratio (length/diameter) ≥ 3 and diameter ≤ 100 µm. Fibres of length < 5 µm need not be considered. Method A, which determines the effective hydrodynamic radius, R_s, will be used for both fibrous and non-fibrous particulates without prior inspection. It is useful only in the range 2 µm < R_s < 100 µm.

- Definitions and units

For Method A the parameter of interest is the effective hydrodynamic radius, or effective Stoke's radius R_s. The terminal velocity of a small sphere falling under the influence of gravity in a viscous fluid is given by:

$$v = 2_g R_s^2 (d_1 - d_2) / 9\eta$$

where:
- v = velocity (m/sec),
- g = gravitation constant (m/sec^2),
- R_S = Stokes radius (m)
- d_1 = density of sphere (kg/m^3),
- d_2 = density of fluid (kg/m^3),
- η = dynamic viscosity (Nsec/m^2 = Pa s) of the fluid.

In other situations, similar relationships apply. Particle size is usually measured in micrometers (= 10^{-6} m).

Method B provides histograms of the length (1) and diameter (d) distributions of fibres. The ordinate is the absolute number of particles in each interval of 1 or d. Typical plots are provided in Figures 1 and 2.

- Reference substances

Five reference substances of defined particle size covering the overall range 0.35 to 650 µm (excepting the 50 to 200 µm region) have been certified with respect to the cumulative mass distribution of particles versus equivalent settling rate diameter or equivalent volume diameter. The materials will be made available from the Community Bureau of Reference* of the European Economic Community and they will be issued with certificates of measurement. The certification report (4) will also be available from the Community Bureau of Reference.

Calibration materials

Method A: A binary or ternary mixture of latex spheres ($2\mu m \leq d \leq 100\ \mu m$) is suggested.

Method B: No standard reference materials are readily available.

Evaluation materials

Method A: A ternary mixture of 2 µm, 50 µm and 100 µm latex spheres (which provides a discrete calibrated distribution) plus a sample of crushed quartz (continuous distribution).

Method B: Fibrous chrysotile asbestos is recommended (specific properties not essential as long as enough of a thoroughly mixed sample is available for identical distribution in a ring test).

- Principle of the test methods

Method A: There are several standard methods available which meet the sensitivity requirements:

Principle	Methods
Sedimentation	ASTM-D 3360, D 422 NF-T 30044 DIN - 66-115

* for addresses: see Annex 2

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Centrifugation	ASTM - C 678 Chem. Ing. Tech. 46, 729 (1974)
Coulter counter	ANSI-C 690-75

The comparability of these methods (especially the sedimentation) and the other methods must be determined.

The sample should also be subjected to a simple light microscopic examination to determine the approximate nature of the particles (e.g. plates, needles, etc.).

Method B: Since data must be collected on small diameter fibres (≥ 0.1 µm), scanning (SEM) or transmission (TEM) electron microscopy is required. There is no standard procedure at present, and those currently under development for asbestos contamination (in which the fibrous material is already identified and in high concentration) are often more complex and expensive than necessary for the needs of this programme. Extreme care must still be taken during sample preparation to avoid fibre breaking, clumping and contamination. A simple initial procedure is suggested below (Description of the test procedures). The length and diameter of the fibre images can be measured manually, semi-automatically or automatically and the results tabulated in histogram form (see Figures 1, 2).

Figure 1: Sample fibre length distribution (Method B)

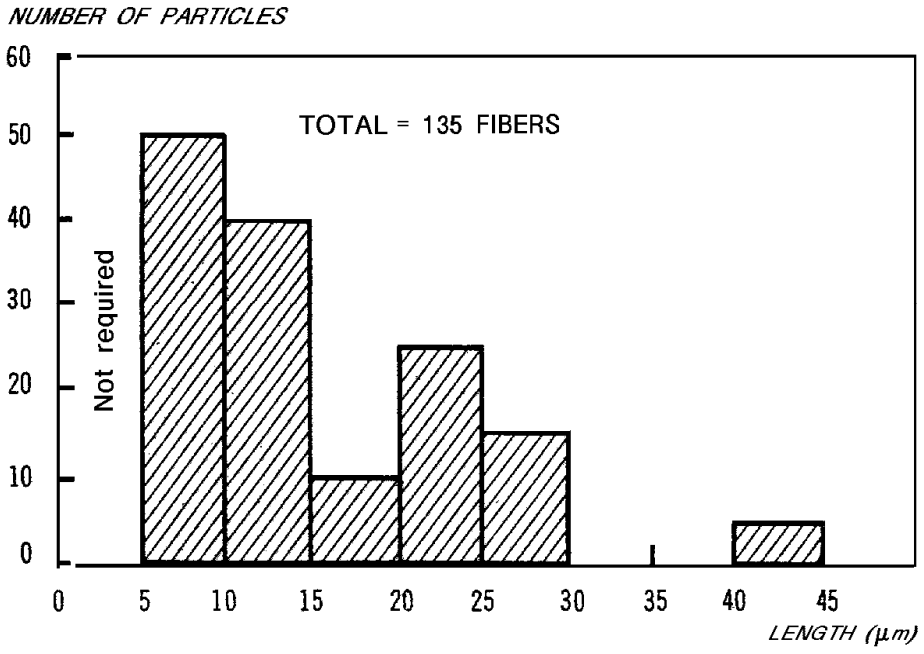
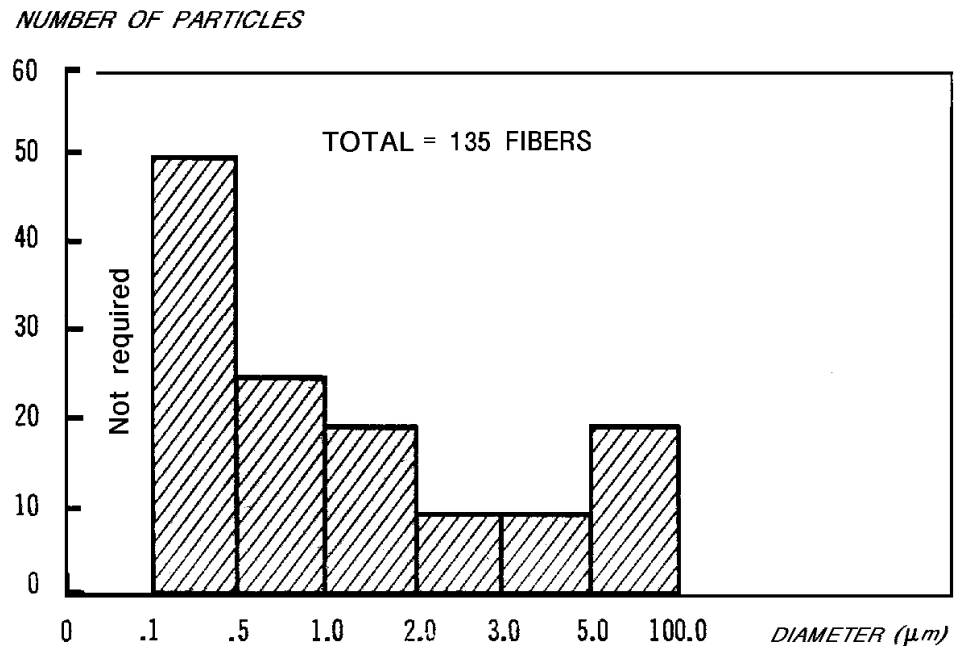


Figure 2: Sample fibre diameter distribution (Method B)



- Quality criteria

Repeatability

The effective hydrodynamic radius distribution (Method A) should be measured three times, with no two values differing by more than 20 per cent.

The length and diameter distributions of fibres (Method B), if required, should be measured at least twice - using separate samplings and preparations - with at least 70 fibres per histogram. No two values in a given histogram interval should differ by more than 50 per cent or 3 fibres, whichever is larger. Such repeatability should be sufficient for the modeling and decision-making procedures currently envisaged; however, the presence of long, thin fibres - due to their potential adverse health effects - would indicate a need for further, more precise measurements.

Sensitivity

In the general case (Method A) particles as small as 2 µm and as large as 200 µm must be measurable. The method requires that sufficient numbers of radius intervals be used to resolve theradius distribution curve. In the case of fibres (Method B), diameters as small as 0.2 µm and as large as 100 m and lengths as small as 5 µm and as large as 300 µm, must be measurable.

Specificity

See Section 2.A, above.

Possibility of standardisation

The method procedures can be readily standardised, if desired, but non-uniformity of sampling, preparation and prior handling may still cause considerable variation in results in Method B.

Possibility of automation

Automation or semi-automation of these procedures is possible. Full automation of fibre 1 and d measurements and analysis is also possible.

B. DESCRIPTION OF THE TEST PROCEDURES

- Preparations

Method A:

The small quantities used as samples must be representative of product batches comprising many kilograms; therefore, sampling and sample handling require great care. For example, small particles often form agglomerates; therefore, sample pre-treatment (e.g. the addition of dispersing agents, agitation, or low-level ultrasonic treatment) may be required before the primary particle size can be determined. However, great care must be taken to avoid changing the particle size distribution. In the case of highly stable aggregates, a strict distinction between primary particles and agglomerates is not always useful. Some representative sample preparation methods will be found in the standard procedures listed in Principle of the test methods (Method A) above.

Method B:

Two simple sample preparation procedures (B-1, B-2) for scanning electron microscopy can be suggested.

Sample preparation B-1

Suspend a given amount of sample in 10-100 ml of filtered distilled or deionised water (the suspension should be relatively light, not a slurry). Distribution of the particles in suspension may be aided by use of a surfactant, such as small amounts (~ 1 part/100) of absolute ethyl alcohol or a non-ionic detergent. Suspension of the powder is achieved by gentle hand agitation, vortex mixing or magnetic stirring. Filter the suspension directly onto a 47 mm diameter Nuclepore* filter overlaying a 47 mm diameter Millipore* membrane filter housed in a 47 mm diameter Millipore* filter holder (Hydrosol, stainless) using gentle vacuum. Ensure that the powder has not precipitated out of suspension. Depending on the size of particles of interest, various pore-sized filters may be used. The concentration of suspended particles determines the amount filtered. A less concentrated suspension will give a more even distribution of particles on the filter surface (2). Remove the Nuclepore filter from the filter housing, being careful not to disturb the particles on the surface. Place the filter - particle-coated face upward - into a glass or plastic Petri dish containing Whatmann* No.1 filter paper; Cover Petri dish and store in a dry box or under vacuum. When completely dried, the filter is cut into pieces of appropriate size and mounted, filter face up, onto copper tape which has been previously mounted onto an SEM specimen holder (using double face tape). To insure stickiness of the tape, preheat using infrared or similar heat source for 5 to 15 minutes. Trim the edge of the filter to fit the SEM specimen holder.

Sample preparation B-2

An alternate sample preparation method is the direct transfer of the dry powder onto copper tape (adhesive electrical tape) which has been mounted onto a scanning electron microscope (SEM) specimen holder. The powder may also be sprayed onto the copper tape surface by using an atomiser or pipette equipped with a large rubber bulb.

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* addresses are listed as indexed in Annex 2.

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- Test conditions and apparatus

Method A: Ambient conditions. Measuring apparatus for all methods are readily available. Pipettes and sedimentation balances are used for the sedimentation methods.

Method B: Contamination by air-borne fibres can be a problem. A hood or "clean room" should be used if available.

A small electron microscope and support equipment are required.

- Performance of the tests

Method A: To be selected from standard procedures listed above (Principle of the test methods).

Method B: Both preparation methods (B-1 and B-2) provide a particulate sample on filter paper or copper tape mounted on an SEM specimen holder. This can then be examined in the SEM, or first coated with metal film using a sputtering device or vacuum evaporator. Representative fields within the sample surface are photographed at various magnifications to yield a representative sample of the population of interest. (If desired, energy dispersive X-ray analysis (EDXA) of representative particles - to check sample contamination - could be performed at this time.)

Particle size distribution can be determined by measuring the screen directly or from measurements on photographs. If the SEM is equipped with an image analysis system, population statistics can be determined directly. Such measurements can be automated or semi-automated when desired (3). If the image indicates the sample is too concentrated, repeat again with a more dilute solution.

- Analysis

Measuring the physical parameters by different methods can result in somewhat different particle size distributions; therefore the measuring techniques used should always be reported. Representative analysis methods are discussed in references 1 - 6.

3. DATA AND REPORTING

Method A: Data should be obtained for 3 size ranges: > 200 µm, < 2 µm and the region 2 to 200 µm. Only in the latter range should the distribution curve be prepared. It should have sufficient µm increments to resolve the curve (subpopulations). A histogram presentation is required plus a statement on the weight per cent of material > 200 µm and < 2 µm.

Method B: Full length (l) and diameter (d) data are needed on fibres of dimensions $d \geq 0.1$ µm and $l \geq 5$ µm. Two histogram distributions, based on examination of at least 50 fibres each, should be prepared. For diameters, the ranges should be 0.1 - 0.5, 0.5 - 1.0, 1 - 2, 2 - 3, 3 - 5 µm and over 5 µm. For lengths they should be 0 - 5, 5 - 10, 10 - 15, 15 - 20, (etc.) µm. This is illustrated in Figures 1 and 2, above.

- Test report

Method A: The following information should be presented:

– Expected per cent change of reported values in the future (e.g. variations between production batches)

– Sample preparation methods used

– Analysis methods used

– Approximate information on particle shape (e.g. spherical, platelike, needle shaped)

– Lot number, sample number

– Suspending medium, temperature, pH

– Concentration

– Stoke's (effective hydrodynamic) radius R_s distribution for $2 \leq R_s \leq 200$ µm

– Mean value and approximate "area" (per cent) of any resolvable peaks in R_s distribution

– Per cent of particles with $R_s \leq 2$ µm

– Per cent of particles with $R_s \geq 200$ µm

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Method B: The following information should be presented:

– Sample description, method description

– Number of particles per field

– Total number of fibres measured

– 1, d distributions (histograms)

– Mean value and approximate "area" (percent) of any resolvable peaks in the R_s distribution.

4. L I T E R A T U R E

1. T. Allen, *Particle Size Measurement*, Chapman and Hall, London (1975).

2. R.R. Irani and C.F. Callis, *Particle Size Measurement*, Interpretation and Application.

3. S. Orr and J.M. Dallavalle, Fine Particle Measurement.

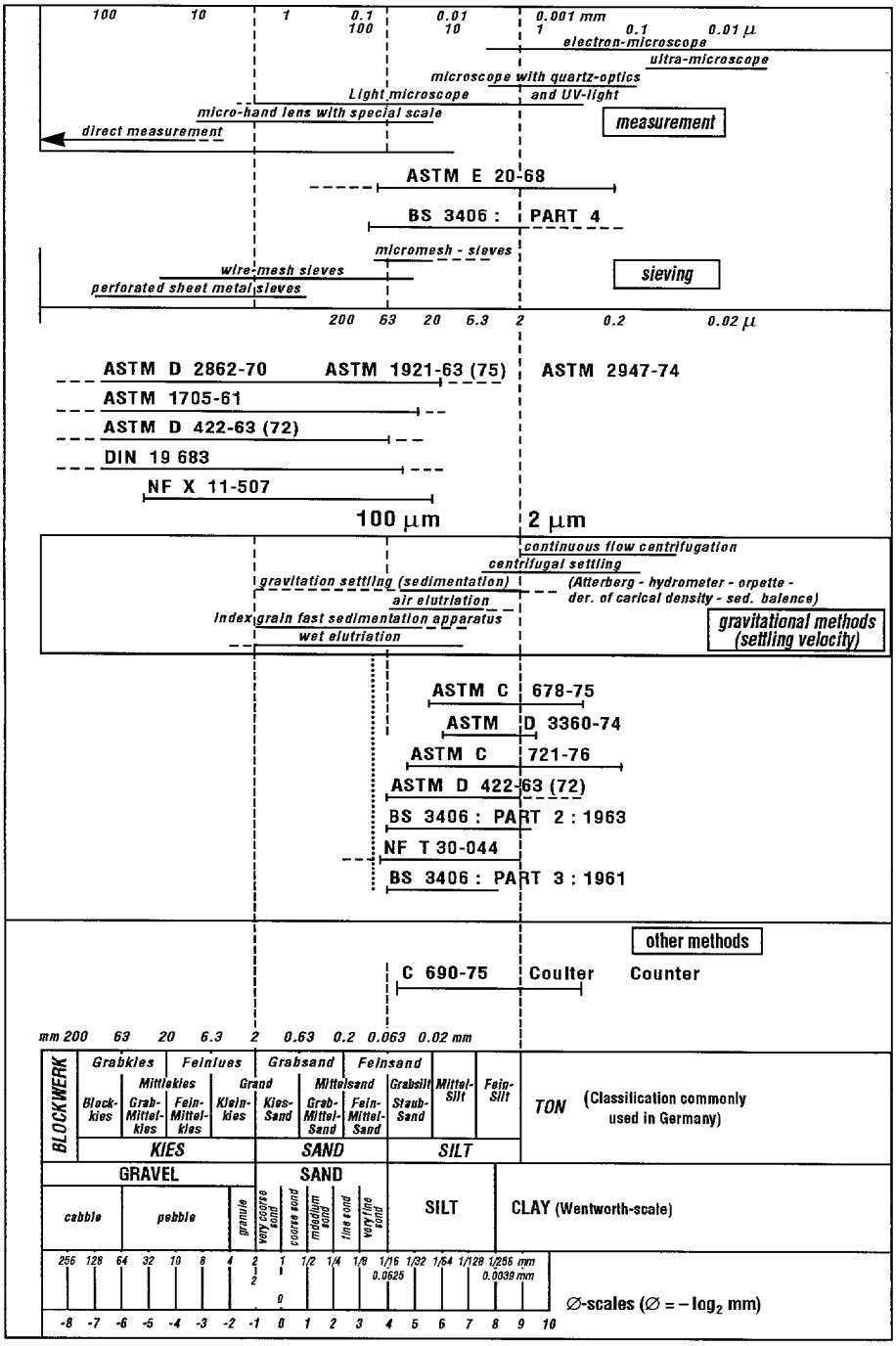
4. Certification Report on Particles of Defined Particle Size, Community Bureau of Reference, Brussels (1979).

5. P.P. McGrath and J. B. Evell, Application of Electron Microscopy to Problem of Particulate Contaminants in Food, Drugs and Biologicals, *Scanning Electron Microscopy*, Part III, 1976.

6. *Symposium on Electron Microscopy of Microfibers*, edited by I.M. Asher and P.P. McGrath, Proceedings of the First FDA Office of Science Summer Symposium, (August 23-25, 1976).

5. A N N E X

1. SUMMARY OF THE USUAL METHODS FOR THE DETERMINATION OF PARTICLE SIZE AND THE IMPORTANT GRANULAR SIZE CLASSES, (according to G. Müller, *Methoden der Sedimentuntersuchungen*, 1964, p. 303, Stuttgart, revised with appropriate supplements).



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2. ADDRESSES

The certification report of five reference materials will be available from:

Commission of the European Community
Directorate - General for Research
Science and Education
Community Bureau of Reference BCR
rue de la Loi 200
B-1049 Brussels

Filter equipment for sample preparations according to Method B is available commercially through the manufacturers listed below:

Nuclepore Corporation
7035 Commerce Circle
Pleasanton
California 94566/USA

Millipore Corporation
Order Service Department
Bedford
Massachusetts 01730/USA

Whatman Filters
W & R Balston Limited
England