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Determination of particle size distributions — Electrical sensing zone method

Détermination des répartitions granulométriques — Méthodes de la zone de détection électrique

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 13319 was prepared by Technical Committee ISO/TC 24, *Sieves, sieving, and other sizing methods*, Subcommittee SC 4, *Sizing by methods other than sieving*.

Annexes A to E of this International Standard are for information only.

Determination of particle size distributions — Electrical sensing zone method

1 Scope

This International Standard gives guidance on the measurement of the size distributions of particles dispersed in an electrolyte solution using the electrical sensing zone method. It does not address the specific requirements of the particle size measurement of specific materials. The method described in this International Standard measures particle volumes and reports in the range about from 0,6 μm to 1 600 μm.

2 Terms and definitions

For the purposes of this International Standard, the following terms and definitions apply.

2.1
dead time
time during which the electronics are not able to detect particles due to the signal processing of a previous particle

2.2
orifice
small-diameter hole through which suspension is drawn

2.3
sensing zone
volume of electrolyte solution within, and around, the orifice in which a particle is detected

2.4
sampling volume
volume of suspension that is analysed

3 Symbols

D	orifice diameter, in μm
K_d	calibration constant of diameter
$\overline{K}_d$	calibration constant of mean diameter
$\sigma_{\overline{K}_d}$	standard deviation of mean calibration constant
m	mass of sample in beaker, in g
V_T	volume of electrolyte solution in which m is dispersed, in ml
V_m	analysis volume, in ml
ΔN_i	number of counts in a size interval i
ρ	mass of the particles per volume of the electrolyte it displaces, in g·ml^{-1}
$\overline{V}_i$	arithmetic mean volume for a particular size interval i, in ml

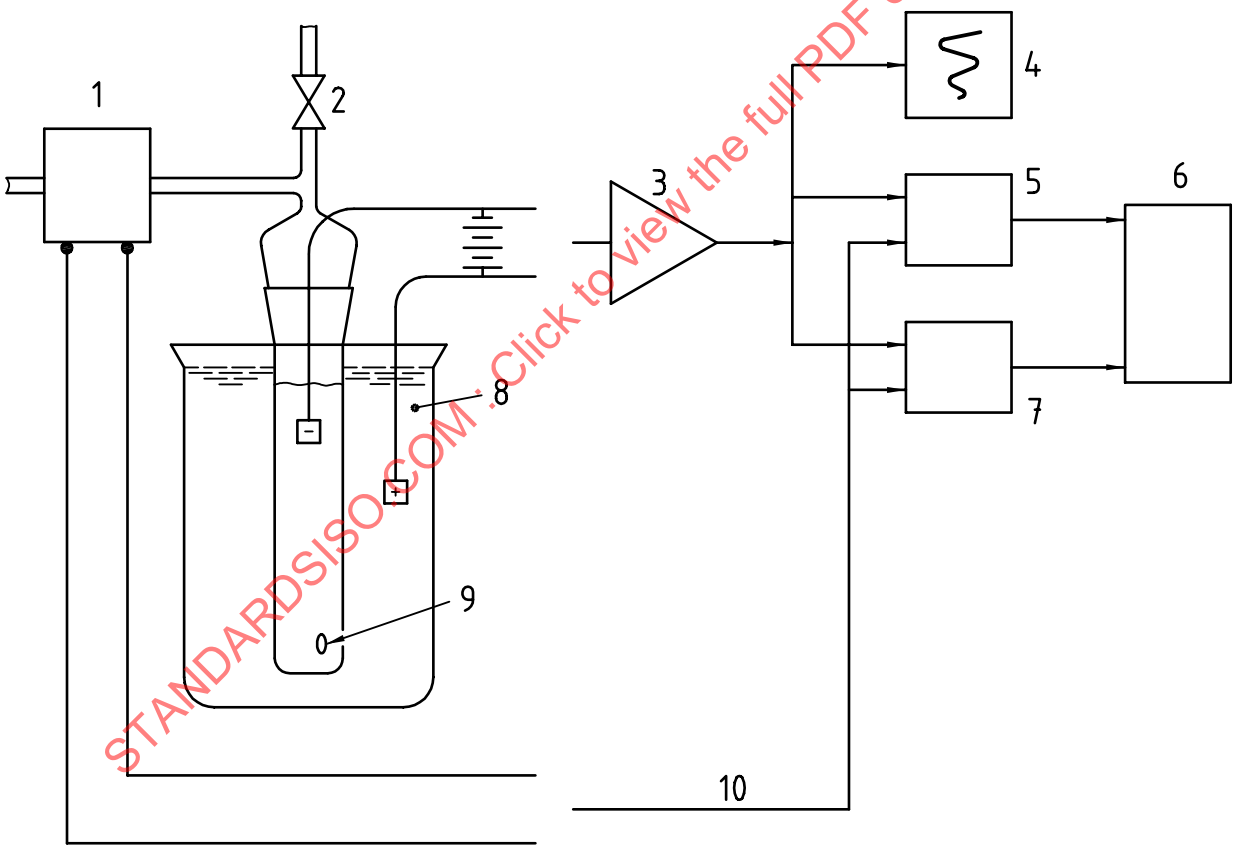
V_i volume of the particle obtained from the threshold, or channel boundary and instrument units; without an arbitrary calibration to particle diameter (i.e. $V_i = tIA$, where t = threshold level, I = current through aperture and A = attenuation factor), in ml

x diameter of a sphere with volume equivalent to that of the particle, in μm

x_{50}, x_{10}, x_{90} the values of x corresponding to the 50 %, 10 % and 90 % percentile points of the cumulative per cent undersize distributions, in μm

4 Principle

The response, i.e. the electrical pulse generated when a particle passes through the orifice, has been found both experimentally and theoretically to be proportional to the particle volume (see Bibliography). A dilute suspension of particles dispersed in an electrolyte solution is stirred to provide a homogeneous mixture and is drawn through a small orifice, or aperture, in an insulating wall. A current applied across two electrodes, placed on each side of the orifice, enables the particles to be sensed by the electrical impedance changes as they pass through the orifice. The particle-generated pulses are amplified and counted and the pulse height is analysed. After employing a calibration factor, a distribution of the number of particles against the volume-equivalent diameter is obtained. This distribution is usually converted to percentage by mass versus particle size, where the size parameter is expressed as the diameter of a sphere of volume and density equal to that of the particle. See Figure 1.



Key

1	Volumetric metering device	6	Output
2	Valve	7	Pulse-height analyser
3	Pulse amplifier	8	Stirred suspension of particles in electrolyte solution
4	Oscilloscope pulse display	9	Aperture
5	Counting circuit	10	Counter start/stop

Figure 1 — Diagram illustrating the principle of the electrical sensing zone method

5 General operation

5.1 Response

If the particles are spherical, the electrical response is proportional to the volume of the particles. This has also been shown to be true for particles of other shapes; however, the constant of proportionality (i.e. the instrument's calibration constant) may be different. In general, particles should have a low conductivity with respect to the electrolyte solution, but conducting particles can be measured.

5.2 Size limits

The lower size limit of the electrical sensing zone method is generally considered to be restricted only by thermal and electronic noise. It is normally stated to be about 0,6 μm, but under favourable conditions a lower limit is possible. There is no theoretical upper limit, and for particles having a density similar to that of the electrolyte solution, the largest orifice available (normally 2 000 μm) may be used.

When the particle density is high, the upper size limit is reached when the particles can no longer be kept in homogeneous suspension. In this case, the viscosity and/or the density of the electrolyte solution has to be increased, for example by the addition of glycerol or sucrose.

The size range for a single orifice sensor is proportional to the orifice diameter, D. The response has been found to depend linearly on D over a range from 0,015 D to 0,80 D (i.e. 1,5 μm to 80 μm for a 100 μm orifice), although the orifice may become prone to blockage at levels greater than 0,60 D. This range can be extended by using two or more sensors (see annex B) but in practice this procedure can be avoided by the careful selection of the diameter of one sensor, to achieve an acceptable range.

The response of the instrument is dependent on the effective electrical resistance of the particle, which is usually high. The measurement of conducting particles (e.g. metals, carbon, silicon and many types of cells and organisms, such as blood cells) requires more time to implement. The particles can become electrically translucent (i.e. give a smaller electrical pulse than their volume indicates) if a voltage, typically of 10 V to 15 V or more, is applied between the electrodes. To obtain acceptable results, a distribution is obtained under normal conditions. The analysis is then repeated using half the current and twice the gain (1/attenuation). The distributions should be the same. If they are not, the procedure should be repeated using an even lower current.

5.3 Effect of coincident particle passage

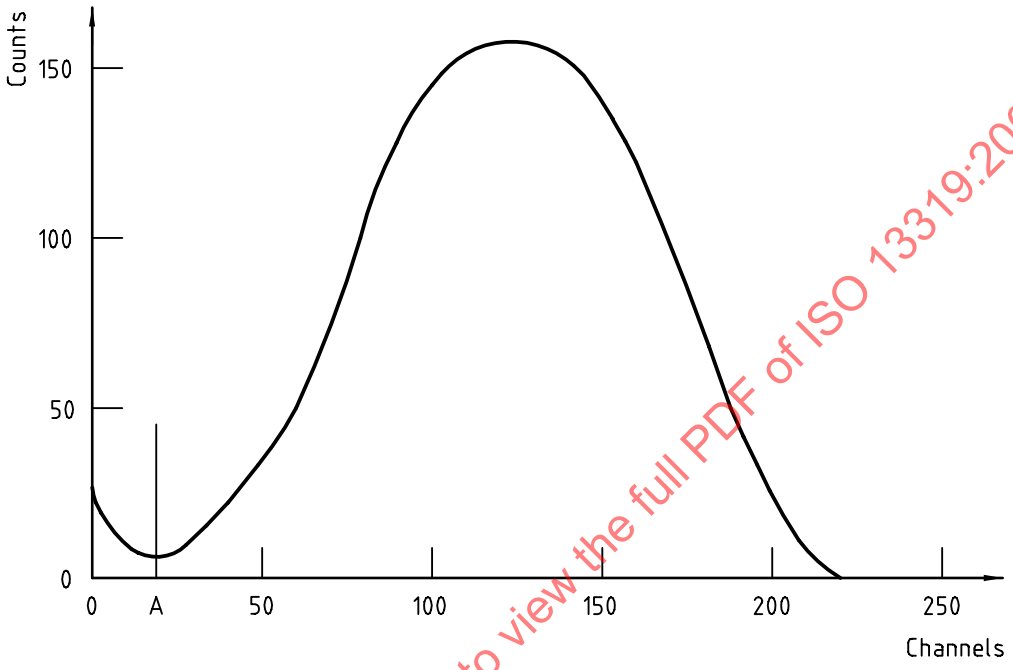
Ideal data would result if particles traversed the orifice singly, when each particle would produce a single pulse. When two or more particles arrive in the sensing zone together, the resulting pulse will be complex. Either a single large pulse will be obtained, resulting in a loss of count and effectively registering a single larger particle, or the count will be correct but the reported size of each will be increased, or some particles will not be counted. These effects will distort the particle distribution obtained but can be minimized by using low concentrations. Table 1 shows counts per millilitre for the coincidence to be 5 % (i.e. approximately only one particle in twenty is affected). Counts per millilitre should always be less than these quoted values. Since particle size distributions should not be a function of concentration, the effect of coincidence can be tested by obtaining a distribution at one concentration and comparing it with that obtained when the concentration is halved. In such a test, repeat such dilutions until the reduction in count in a channel with the largest number decreases in proportion to the dilution. This should always be done when analysing very narrow size distributions, as this is where the effect of coincidence is most noticeable.

5.4 Dead time

In some modern instruments, pulse-height analysis routines are used to process the data. Since it takes a finite time to process each pulse, it is possible that the analyser may not count particles for a given time after receiving a pulse. This means that, for a relatively high count rate, a significant proportion of the counts may be lost. Since dead time is not a function of the pulse height, the loss will be proportional to the counts in each channel and will not affect the size distribution. However, if concentration is to be reported or the mass integration method of calibration (see 6.11.3) is to be used, the effect can be kept to a minimum by using dilute suspensions (e.g. at < 5 % coincidence) and setting up the instrument so that the pulses in the lowest channels are not counted. This is

done by first obtaining a count distribution and observing the number of counts per channel. A typical result is shown in Figure 2. By restricting the counts in the lowest channel to that shown by A, the dead time will be minimized.

In normal operation, this dead time will not cause any distortion of the size distribution since all particles will have the same chance of not being counted, provided that a large number of particles, at least 100 000, are counted. However dead time will affect the accuracy of the mass integration method of calibration (see 6.11.3), when there will be an apparent loss of mass.



Counts at channels below A are noise counts. True particle counts are at the higher channels

Figure 2 — Typical results

5.5 Repeatability of counts

It has been shown that, in a correctly performed analysis, the number of counts in each channel is a random variable which follows Poisson's law. This means that the standard deviation of a number of counts N approximates to $\sqrt{N}$. Thus, in a series of replicate runs the number of counts in a channel, $N_{i,1}$, $N_{i,2}$, $N_{i,3}$, etc., which yield a mean count N_i with 95 % confidence, the replicate counts $N_{i,n}$ should be in the range $N_i \pm 1{,}96\sqrt{N_i}$; i.e. if the count N_i is 100 000, the uncertainty is $\pm$ 619. If 20 replicate analyses yield more than one outside this range, the sample preparation procedure should be re-examined (see 6.7). This statistical test can be performed on single channels, groups of channels, or on the total particle count.

6 Operational procedures

6.1 Instrument location

The instrument should be sited in a clean environment that is free from electrical interference and vibration. If organic solvents are to be used, the area should be well ventilated.

6.2 Linearity of the sensor/amplifier system

The linearity of the sensor/amplifier system can be checked using three monodisperse particles of certified diameter. In a suitable electrolyte solution, the instrument is calibrated with particles at about 0,3D (see 6.11.2). Two further sizes of microspheres are then added to the suspension (one of size $\approx$ 0,2D and one $\approx$ 0,5D). The suspension is re-analysed and the size corresponding to these extra peaks has to correspond to the quoted size of the particles to within 5 %.

6.3 Linearity of counting system

The linearity of the counting system can be tested by obtaining three counts at an arbitrary concentration. The concentration is then reduced and three further counts obtained. The ratio of the mean of the counts should be the same as the dilution. If the agreement is not within 5 %, the test should be repeated comparing the two lowest dilutions; (coincidence may prevent the true count being obtained if the concentration is too high). Subsequent analyses should be carried out at the dilution giving the best results.

6.4 Volume V_m of analysed suspension

If particle concentrations are to be determined or the mass integration method of calibration (see 6.11.3) is to be used, it is necessary to check the volume V_m of the analysed suspension, which is usually only guaranteed at one metered value by the manufacturer. This value of the analysed volume should be known. Using a suspension of particles, at a statistically valid count level (see 6.3), measure the total particle count with that volume three times. Switch to another analysis volume and obtain the total particle counts at least three times. The ratio of the total number of counts will be the ratio of the guaranteed volume to the selected volume. All counts should be recorded.

6.5 Choice of electrolyte solution

An electrolyte solution should be selected in which the sample is stable. The electrolyte solution should not dissolve, flocculate, react or otherwise interfere with the state of dispersion of the sample in the measurement time, typically up to 5 min.

Particles insoluble in water can be analysed in aqueous electrolytes, such as 50 g/l hydrated trisodium orthophosphate solution, or 10 g/l sodium chloride solution. Particles soluble in water can often be analysed in 50 g/l lithium chloride solution in methanol, or 50 g/l ammonium thiocyanate solution in iso-propanol. See annex A for other recommended electrolyte solutions for many common materials.

6.6 Preparation of electrolyte solution

The electrolyte solution should be well filtered with a membrane filter for which the pore size is less than the diameter of the smallest particle measured, as it is essential that its background count should be as low as is practicable. All glassware and other apparatus used should be pre-rinsed with filtered electrolyte solution. Background counts should not exceed the values given in Table 1 or yield a total equivalent volume in excess of 0,1 % of the total volume of particles subsequently measured in the same sampling volume.

Table 1 — Counts for background and 5 % coincidence for typical orifice diameters

Orifice diameter D µm	Analysis volume [a] V_m ml	Background counts [b]	Count for 5 % coincidence [c] N
1 000	2	2	80
560	2	10	455
400	2	25	1 250
280	2	75	3 645
200	2	200	10 000
140	2	600	29 150
100	0,5	400	20 000
70	0,5	1 200	58 300
50	0,05	300	16 000
30	0,05	1 500	74 000
20	0,05	5 000	250 000

a For other sampling volumes, use *pro rata* values.

b Suggested maximum counts.

c Calculated using the equation $N = \frac{4 \times 10^{10} V_m}{D^3}$

6.7 Recommended sample preparation and dispersion

6.7.1 General

A dispersant should be selected from the recommendations in ISO 14887 or annex A.

6.7.2 Method 1: Using a paste

The sample should be subdivided to about 0,2 cm^3. If the sample is in the form of a powder, it should be worked and kneaded gently with a flexible spatula with a few drops of suitable dispersant to break down agglomerates. A mass of about 20 mg to 50 mg of the paste is transferred into a round-bottomed beaker and thinned with dispersant, followed by a few drops of electrolyte solution. The beaker is nearly filled with electrolyte solution and placed in a low-power ultrasonic bath for 1 min, stirring occasionally. A suitable design of beaker of 400 ml capacity with a baffle is shown in Figure 3. The ultrasonic bath should be in the range 50 W to 100 W, 60 kHz to 80 kHz, and a stop watch is recommended for a reproducible dispersion technique.

NOTE The use of high-energy ultrasonic baths and probes, blenders and mixers can cause both agglomeration and fracture of particles.

If the sample is not required to be fully dispersed, it may be added to the electrolyte solution and dispersant while stirring.

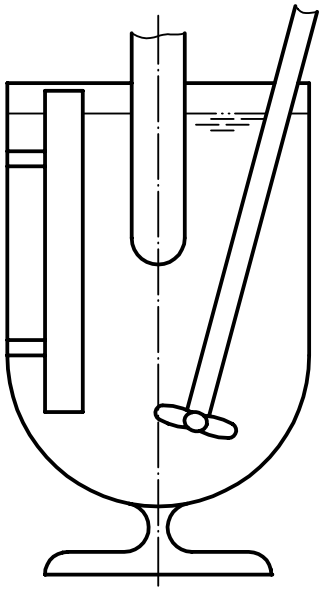


Figure 3 — Example of a beaker with baffle and stirrer

6.7.3 Method 2: Alternative method applicable to low-density particles of less than 50 μm

The sample should be subdivided to about 1 g of the sample. This is mixed with the dispersant and is added to the electrolyte and solution. The beaker (see Figure 3) containing the suspension is then placed in an ultrasonic bath for about 45 s. After stirring this stock suspension well, 5 ml is withdrawn using a pipette and is added to approximately 400 ml of electrolyte solution and placed in the ultrasonic bath for a further 15 s. When using this method, it is important that at least two samples are withdrawn from the stock suspension and analysed to ensure repeatability of the aliquot sampling and the analysis.

6.7.4 Suspensions and emulsions

Suspensions and emulsions may be diluted by slowly adding electrolyte solution. To avoid “dilution shock”, oil-in water emulsions may be initially diluted with distilled or de-ionized water.

6.7.5 Verification of the dispersion

A small sample of the dispersion may be placed on a microscope slide and used to verify the degree of dispersion and to estimate the size range of the particles.

6.8 Choice of orifice(s) and sampling volume(s)

From the microscope examination (6.7.4), estimate the diameter of the largest particles present.

Choose an orifice for the size analysis such that the diameter of the largest particles to be analysed is less than approximately 50 % of the diameter of the orifice, selected to reduce the possibility of blocking the orifice . If there is a considerable proportion of sample below the lower size limit of that orifice (1,5 % of its diameter), a second and possibly a third smaller orifice will be needed (see annex B).

Select a suitable sampling volume with reference to Table 1. It may be necessary to analyse a number of these sampling volumes to accumulate a statistically valid total number of particles, for example about 100 000 [i.e. a precision of ± 619 (see 5.5) or better than ± 1 %]. Counting fewer particles will reduce the precision, but this may be necessary when using the larger orifices or performing contamination studies.

6.9 Clearing an orifice blockage

Orifices below 100 μm in diameter may become blocked with extraneous particles, particularly if care is not exercised in the clean handling, careful filtration, and thorough rinsing of beakers and associated equipment. A blockage is readily seen by means of the viewing optics provided with the analyser.

A partial blockage may be indicated by different flow times for the same metered volume. Blockages can be removed automatically or by one of the following techniques:

a) Back flushing: Reversing the flow through the orifice may be sufficient to clear a blockage.

b) Boiling: It is possible to use the heating effect of the current to boil the blockage out. This is done by using a high orifice current.

c) Brushing: It is often possible to brush the particles off the orifice by using a small high-quality soft-hair brush with the hairs cut short. Care should be taken not to damage the orifice.

d) Air pressure.

e) Ultrasonic cleaning: With the orifice tube filled with electrolyte solution, the end is dipped into a low-power ultrasonic bath for about 1 s. Repeat this operation as necessary. This method is very effective but extreme care should be taken as it is possible to damage the orifice.

Caution — This method should not be used for orifices of 50 μm or less.

6.10 Stability of dispersion

With the most suitable orifice fitted, and the suspension prepared, dry the outside of the beaker and place it on the sample stand of the instrument. Adjust the stirrer for maximum effect without creating a vortex which will entrain bubbles.

The stability of the dispersion during the analysis time is then checked. A full size analysis is made as soon as possible after dispersion; the suspension is then stirred for 5 min to 10 min and finally is reanalysed. Cumulative counts are recorded at size levels close to 30 % and 5 % of the orifice diameter (denoted x_{max} and x_{min} respectively). Changes in the counts greater than those expected from statistics, i.e. $\sqrt{N}$, will indicate that the dispersion is not stable. Table 2 details some possible causes.

Table 2 — Examples of suspected phenomena in dispersion

Change in count at		Suggests
x_{max}	x_{min}	
no change	no change	Stable dispersion
increase	increase	Crystallization, precipitation
decrease	decrease	Dissolution
decrease	increase	Size reduction, deflocculation
increase	decrease	Flocculation, agglomeration
decrease	no change	Settling of large particles

In all but the first case given in Table 2, a different dispersant/electrolyte solution combination should be tried, and the dispersion rechecked.

6.11 Calibration

6.11.1 General

Electrical sensing zone instruments are usually calibrated using polymer latex microspheres of known size and narrow size distribution. However, the mass integration method (6.11.3) is generally believed to be closer to an absolute method. Here the volume concentration of the suspension as determined by the instrument is compared to the true volume concentration determined from the mass per unit volume and the immersed density of the particles. This calibration method is directly traceable and there is no assumption made about the shape, porosity or electrical conductivity of the particles. Unfortunately, some instruments have a dead time in the pulse-processing circuitry which can be significant and can correspond to an effective loss in the mass of the particles analysed. This loss will depend on the total number of particles counted, but does not affect the size distribution obtained since the same proportion of the count will be lost for all size classes.

Calibration should be checked on a regular basis to ensure that the change in the calibration constant is less than 1,0 %, or every time an orifice tube or an electrolyte solution is changed. See annex D for a method for calibration of frequently used orifices.

6.11.2 Calibration procedure: microsphere calibration

Microspheres of narrow size distribution with a single mode, characterized by a variety of other methods, are available. They should be traceable to the micrometre, to a Community Bureau of Reference (BCR), a National Institute of Standards and Technology (NIST) or similar reference material. The calibration method used depends on the assayed size parameter of the microspheres and the analyser used (contact the instrument manufacturers for details). One method is to obtain a histogram (frequency) plot of the number of particles against channels of equal width (on a linear scale). The size at the centre of the channel with the greatest number of particles corresponds closely to the modal size of the calibration material if the distribution is symmetrical. If the distribution is not symmetrical, the fractional channel position is calculated from the counts in the channels on either side of the central channel. The calibration factor is the ratio of the modal size of the calibration material to the size as reported on the instrument.

6.11.3 Calibration procedure: mass integration method (self-calibration)

6.11.3.1 A narrow size-range fraction of the material under test is prepared by sieving or a similar separation method. At least 99 % of the mass of the particles should lie within a size range of no more than 10:1, so that all can be measured using one orifice.

6.11.3.2 Using a balance weighing to an accuracy of 0,1 mg, a relative-density bottle, pipettes and the usual particle-dispersion method, the immersed density ρ_s of the material in the electrolyte solution to be used for the analysis is determined.

6.11.3.3 A suspension is prepared by dispersing a mass m_g of the powder in a volume V_T of the electrolyte and dispersing agent.

6.11.3.4 The calibration factor K_d for the instrument is then determined by measuring very carefully the size distribution using an accurately known sampling volume, V_m, ensuring that the orifice is absolutely clear. A number of sampling volumes may be counted so that the total number of particles is in excess of 100 000. The particle concentration used should be much less than the 5 % coincidence limit.

K_d is calculated from the formula

$$K_d^3 \left(\frac{\pi}{6} \times \frac{\sum \Delta N_i \overline{V_i}}{V_m} \right) = \frac{m/\rho_s}{V_T} \qquad (1)$$

6.11.3.5 For the results to be accurate it is not sufficient to accept the nominal value of the analysis volume V_m. This should be measured relative to the certified analysis volume as described in 6.4 or the apparatus returned to the manufacturer for accurate measurement. For an example of the calculation, see annex C.

6.11.4 Mass integration using a multi-channel instrument

An alternative mass integration method uses summations available with the instrument. The applicable size range is selected on the instrument and an analysis made on the sample prepared according to 6.11.3. Using the histogram display of the number of particles, the total number of particles, $\sum N_i$, is obtained and using the histogram of the volume of particles, the total volume of the particles, $\sum V_i$, is obtained. The average "instrument" volume, V_{mp_i}, of the particles is given by

$$V_{\mathrm{mp}_i} = \frac{\sum V_i}{\sum N_i} \tag{2}$$

The true average volume, V_{sa}, of the particle is now calculated from the mass, m_{a} of particles in the sampling volume, the density of the particles and the total number of particles:

$$V_{\mathrm{sa}} = \frac{m_{\mathrm{a}}}{\rho \sum N_i} \tag{3}$$

The instrument volume V_{mp_i} is now set equal to the true volume V_{sa}.

For an example of this calculation, see annex C.

6.11.5 Secondary calibration

It is not necessary to perform the full mass-integration calibration procedure for every analysis or for every orifice. It is recommended that, having calibrated for the orifice and material under test, a secondary standard, such as a microsphere suspension, is analysed and used as an intermediate standard to calibrate other orifices within their linear range (see 6.11.2) and for regular checks of stability of calibration.

Analyses reported using this secondary calibration should be identified.

7 Calculation of results

Most analysers count the numbers of particles above, or between, variable equivalent-volume particle diameters, and therefore conversion of data to volume percentage may be required. A few models measure the volume within varying size channels directly, so no data conversion is needed.

In the event of requiring number data to be converted to, and presented as, volume data, it is usual for the method of Simpson's rule to be used. Since the volume of each particle is measured, the numbers of particles within a size interval (size channel) can be multiplied by the arithmetic mean volume of the channel in order to present the total particle volume within the channel. In this way, the total volume of all particles within all size channels can be calculated, and the percentage by volume size distribution calculated. For the calculation to be reasonably accurate, the size interval should be narrow, i.e. a large number of channels should be counted. For a more accurate method and the calculation of moments of the distribution, see ISO 9276-3. Modern analysers perform the calculation automatically.

The volume-percentage distribution so calculated is identical to the mass (or weight) distribution if all of the particles have the same specific gravity (immersed density).

8 Analysis

Most powders have a particle size range that is sufficiently narrow for a satisfactory analysis to be carried out using one orifice. Where the size range of a powder is too wide for a single orifice, two or more orifices should be used. If over 2 % by volume of the particles fall in the smallest size interval, it is advisable to use the multiple sensor method. See annex B.

When the particles are dispersed satisfactorily, following the foregoing procedures, the analysis can begin. By selecting the sampling volume, or by repeating the sampling volumes, at least 100 000 particles are counted to obtain a statistically representative distribution (this may be difficult for larger orifices when the largest number of particles possible should be counted). It is preferable that at least three, and preferably five, replicates be measured. To ensure that the sample subdivision has been carried out well, the whole procedure should now be repeated with at least one other, but preferably more, sample(s) from the stock suspension or from the dry-powder subdivision. Report all the measured data on a data sheet (e.g. that in annex E).

9 Validation

Primary validation can be made with any suitable certified reference material. The total measurement procedure is examined when the reference material is analysed, including the sampling, the sample dispersion, the measurement and the subsequent analysis. It is essential that the whole validation procedure be described in full detail.

Certified reference materials consisting of a known distribution of particles of over one decade of size and certified to the mass percentage undersize versus size by the electrical sensing zone or other method should be used. The validation procedure will meet this International Standard if the mean value of the x_{50}, x_{10} and x_{90}, obtained from three independent measurements lies within the certified range of values of the reference material. If the reference material has not been certified using the electrical sensing zone method, the x_{50} value should deviate less than 3 % from the certified value and the x_{10} and x_{90} values deviate by less than 5 % from the certified values.

Annex A
(informative)

Table of materials and electrolyte solutions

A.1 Key to electrolyte solutions

NOTE 1 Unless otherwise stated, the electrolytes are dissolved in water.

NOTE 2 Salts and solvents for non-aqueous use should be water-free.

a 10 g/l sodium chloride solution (often interchangeable with b)

b Isoton II (often interchangeable with a)

c 4 g/l sodium hydroxide solution

d 0,1 mol/l hydrochloric acid solution (+ 1 g/l cetrimide)

e 20 g/l to 50 g/l trisodium orthophosphate dodecahydrate solution or 20 g/l to 50 g/l sodium pyrophosphate decahydrate solution

f 200 g/l sodium chloride solution

g 10 g/l sodium nitrate solution

h 40 g/l zinc chloride solution

i 20 g/l to 50 g/l sodium sulfate solution

j 10 g/l potassium silicate solution

k 80 g/l ammonium thiocyanate in dimethylformamide

l 50 g/l lithium chloride in methanol (often interchangeable with m)

m 50 g/l ammonium thiocyanate or magnesium perchlorate in propan-2-ol (often interchangeable with l)

n 50 g/l ammonium thiocyanate or lithium chloride in acetone

p 100 g/l to 400 g/l lithium iodide in butan-2-ol

q 40 g/l to 50 g/l ammonium thiocyanate in butan-2-ol

r 40 g/l to 50 g/l lithium iodide in acetone

s 78,5 g/l sodium silicate solution

t 10 g/l sodium carbonate solution

u 60 g/l ammonium thiocyanate in dimethylformamide

v 40 g/l ammonium thiocyanate (in ethanol) + 5 % (volume fraction) formamide

w 2,23 g/l sodium pyrophosphate decahydrate solution

x 100 g/l sodium chloride in 85 % (volume fraction) propan-2-ol in acetonitrile)

y 8 g/l sodium hydroxide solution

z 7 g/l hydrochloric acid solution

aa 80 g/l ammonium thiocyanate in 33,3 % (volume fraction) methanol in propane-1,2-diol

bb 60 g/l lithium iodide in bis(2-hydroxyethyl)ether

cc 50 g/l ammonium thiocyanate in 50 % (volume fraction) methanol in cyclohexane

dd 3 g/l sodium chloride solution

ee 40 g/l ammonium thiocyanate in 70 % (volume fraction) propan-2-ol in dichloroethane

ff 100 g/l concentrated hydrochloric acid in propan-2-ol

gg 40 g/l ammonium thiocyanate in butanone

hh 40 g/l ammonium thiocyanate in dimethylformamide

ii 50 g/l ammonium thiocyanate in 33,33 % (volume fraction) of dimethylformamide, tetrahydrofuran and trichloroethylene

jj 45 g/l lithium chloride in 90 % (volume fraction) acetone in methanol

kk 10 g/l potassium chloride in 90 % (volume fraction) formic acid in water

ll 7,5 g/l ammonium thiocyanate in 90 % (volume fraction) butanone in trichloroethylene

mm 40 g/l ammonium thiocyanate in 50 % (volume fraction) propan-2-ol + 40 % (volume fraction) chloroethane + 10 % (volume fraction) sample

nn 38 g/l lithium in 50 % (volume fraction) propan-2-ol in benzene

oo 100 g/l ammonium thiocyanate in 50 % (volume fraction) propan-2-ol in dichloromethane

pp 10 g/l hydrochloric acid in cyclohexanol

qq Up to 250 g/l lithium iodide in 50 % (volume fraction) propan-2-ol in trichloromethane

rr 50 g/l ammonium thiocyanate in 33,33 % (volume fraction) of propan-2-ol, trichloroethane and tetrahydrofuran

ss 50 g/l ammonium thiocyanate in 33,33 % (volume fraction) of dimethylformamide, trichloroethane and tetrahydrofuran

tt 40 g/l tetrabutyl ammonium perchlorate in 50 % (volume fraction) propan-2-ol in dichloroethane

uu 60 g/l ammonium thiocyanate in bis(2-methoxyethyl)ether

vv 40 g/l ammonium thiocyanate in 83 % (volume fraction) butanone in light petroleum

ww 40 g/l potassium nitrate solution

xx 40 g/l tetrabutyl ammonium perchlorate in dimethylformamide

yy 65 g/l sodium acetate in 66,7 % (volume fraction) ethanol in water

yz 30 g/l lithium chloride in 50 % (volume fraction) propan-2-ol in methanol

zz Karuhn's medium

A.2 Materials and recommended electrolyte solutions

NOTE 1 Where more than one electrolyte solutions are given, they are indicated in preferential order.

NOTE 2 +G signifies that the addition of glycerol can often help suspend large particles.
+S signifies that the addition of sucrose can often help suspend large particles.
satd. signifies that electrolyte solution should be presaturated with sample.

Material	Electrolyte solutions (see A.1)	Comments
Acetylsalicylic acid	a satd., b satd.	Aerosol OT dispersant.
Acrylic emulsion or powder	a, b, e	See chemical name.
Aldactone A	a, b	(Spironolactone.)
Alumina	e	Any aluminas.
	a, b	Coarse powders only.
Aluminium	a	Alkaline electrolyte solutions react.
Aluminium oxide	–	See alumina.
Aluminium silicate (Andalusite)	e	
Ammonium perchlorate	q satd., m	Common ion effect depresses solubility.
Ammonium phosphate	m	Up to 80 g/l ammonium thiocyanate may be used to increase the common ion effect.
Amphotericin (B)	a satd. b satd.	
Anionic bitumen emulsion	c	
Antimony	a	Daxad has been used as dispersant.
Asphalt emulsion	–	See anionic or cationic bitumen emulsion.
Attapulgite	e	
Avicel (microcrystalline cellulose)	a	
Azodicarbamide	m	Slightly soluble in water.
Ball clay	–	See clay.
Barium ferrite	r	See ferrites.
Barium sulfate	i	Common ion effect supresses solubility.
Bark	a	
Barytes	e	
Bauxite	a	
Beef extract (dried)	m	
Bentonite	e	

Material	Electrolyte solutions (see A.1)	Comments
Benzoic acid	b	
Benzyl procaine penicillin	a satd.	
Beryllia	e, a, b	
Bitumen emulsion	–	See anionic bitumen or cationic bitumen emulsion.
Bone	e	
Boron carbide	a, b	Electrolyte solution has been presaturated with boric acid.
Brick dust	l	
Bronze	s, t	The recommended electrolyte concentration should not be exceeded because of chemical attack.
Cadmium sulfide	e	
Calamine	e	
Calcined magnesia	–	See magnesia.
Calcite	–	See calcium carbonate.
Calcium carbonate	l, m, a satd.	
Calcium chromate	l satd.	
Calcium dihydrogen phosphate	l	
Calcium oxide	l	
Calcium stearate	l, a, b, e	Difficult to wet; alcohols, or non-ionic dispersant with ultrasonics and spatulation, has been used.
Calcium trihydrogen phosphate	l	
Carbon (and carbon black)	e, a	Activated carbon will release gases during passage through the orifice to give spurious results. Disperse the powder in a little warm glycerol with a spatula, add a little electrolyte solution and boil for a few minutes. Cool, add the remainder of electrolyte solution and count. Dispersion under vacuum was used.
Carbonyl iron	a(+G), b(+G)	
Carbonyl nickel	a(+G), b(+G)	
Carborundum	–	See alumina and emery.
Casein	m	
Cationic bitumen emulsion	d	
Cellulose	n, m	n is generally more suitable, but it cannot be used unless the flow rate is reduced, with orifices above 280 μm, owing to whistling high-frequency noise interference on rapid flow through the orifice and/or vapour bubble formation in the orifice.
Cement	l, m	
Ceramic powders	e	
Cerium oxide	e	

Material	Electrolyte solutions (see A.1)	Comments
Chalk	–	See calcium carbonate.
China clay (kaolin)	–	See clay.
Chloramphenicol	a satd.	
Chocolate	m satd.	Melt in beaker over water bath at 40 °C to 50 °C, spatulate with 50 g/l alcohol-soluble fraction of Span 80 in cyclohexanol. Cool and add electrolyte solution. Presaturation with defatted solids (from petroleum ether) is essential for milk-chocolate analysis, and sucrose may be used for dark chocolate.
Chromium powder	e	
Clay	e	Usually very fine, it is suitable for 30 μm or 50 μm orifices. It is common to make up a dispersion and leave for one or two days before analysis. When the mass integration method is used, the density should be measured for the material suspended in the same electrolyte solution for a similar time; this is because of water present in the lattice structure.
Coal	e, a, b, m, w	
Cocoa	l	
Coffee	l, m	For powder from coffee beans only.
Coke	a, b, e	
Copper	a, b	No reaction during time for analysis.
DDT	a satd., e satd.	
Diamond	e(+S), b(+S)	
Diatomite	–	See clay.
Dolomitic lime	l	
Dust (flue, coal, etc.)	e, a, b	e is a better choice if metal particles are suspected in the sample, e.g. gas mains dust.
Electrolyte solutions (particles in)	–	To measure particles in electrolyte solutions, e.g. plating solutions, measure directly, or if the particle size range is reduced because the orifice resistance is too low, dilute with filtered distilled water.
Emery	a(+G), b(+G)	Usually in very narrow size ranges, e.g. 75 μm to 85 μm.
Emulsions (including lubrication and coolant emulsions for rolling mills)	a, b	Solids or oil in water can be measured. Two-stage dilution of, for example, 1:100 for each stage is preferable to reduce coagulation. The stability of emulsion over the analytical period should be maintained. NOTE Measurement of water in oil is not possible at present.
Encapsulated particles	l, m	Dependent on encapsulant material.
Explosives: HMX, PETN, RDX	a satd.	See also ammonium perchlorate and guanidine

Material	Electrolyte solutions (see A.1)	Comments
		perchlorate.
Feldspar	a, b	
Ferrites	e	Addition of 500 g/l glycerol reduces re-agglomeration rate.
		Heat-treated ferrites are magnetic and cannot be dispersed to primary particles; the agglomerate size will be fairly stable (1 μm to 20 μm) and measurable and it is preferable to measure before heat-treatment.
Fibres (paper pulp)	a	
Fibres (wool top)	m, x	
Fibres (in glycerine)	b	
Filters	–	See membrane filters.
Flint	a, e	
Flour	m, l	Usual range 10 μm to 125 μm; disperse by spatulation in anhydrous electrolyte solution, then use ultrasonics.
Fly ash	w	
Fullers, earth	e	
Garnet	e	
Glass powder	a, b	Almost any electrolyte solution may be used.
Gold	a, b, e, g(+G)	
Graphite	e	Satisfactory for coarse graphites; very slow flocculation at 1 μm level.
	y	For fine graphite.
Graphite in oil	–	See oil.
Griseofulvin	a satd.	Add 0,1 g/l Goulac for dispersion.
Gypsum	m	
Guanidine perchlorate	q	
Herbicides	a, b	Usually insoluble.
Indomethacin	z satd.	
Injection fluids (particles in parenteral fluids)	–	Usually need no added electrolyte solution. If no electrolyte is present, add filtered sodium chloride solution. Iron dextran apparently has never been analysed successfully, possibly because of complex formation giving unstable counts.
Ink, ball point	aa	
Ink, silk screening	m, bb	
Ink, in toluene	cc	All particles are very fine; many particles are not measurable. Highly coloured suspensions make

Material	Electrolyte solutions (see A.1)	Comments
		observation of orifice difficult.
Ink, printing	zz	
Ion-exchange resin	a, f	Saturate sample in electrolyte solution f to exhaust resin before analysing.
Iridium	e(+S)	Extremely dense (22 g/cm^3): with 500 g/l added sugar, analyses can be performed up to 60 μm to 80 μm.
Iron	dd(+G), e	
Iron oxide	a(+G), b(+G)	
Kaolinite	–	See clay.
Kerosene (paraffin) (particles)	ee	Add up to 20 % (volume fraction) kerosene.
Ketchup (catsup)	a, b	It has been reported that the electrical sensing zone method may not respond to envelope volume for tomato cells.
Latex (rubber)	a, b, e	
Latex (synthetic)	a, b, e	
Lead	a(+S), f(+S)	Methanol has been used as a dispersant.
Lead(II) oxide and lead(III) oxide	a(+G)	Up to 250 g/l glycerol has been used.
Lead, red	e	
Lignite dust	e	
Lime	a satd., l, m	
Lycopodium powder	a, b	
Magnesia	m, l	Reactive in water when finely divided.
Magnesia, calcined	e(+G)	
Magnesium	e(+S)	Very slow reaction; will not affect accuracy of results in usual analytical time.
Magnesium hydroxide	p, e satd.	
Membrane filters		See particles captured by membrane filters.
Mica	e, a, b	
Molybdenum disulfide	y, e	
	m	More suitable for MoS_2 in oil.
Mud	a, b, e	
Neomycin	l satd.	
Nickel	a	See also Raney nickel.
Nylon, particles in	kk	Wet first with dispersant, then add electrolyte solution.

Material	Electrolyte solutions (see A.1)	Comments
Ocean sediment	–	See sediment.
Oil, cutting	a, b	
Oil, hydraulic and lubricating	ll	Will accept up to 50 % (volume fraction) of added oil (DTD 585).
(Oil specifications are for lubrication effectiveness, not composition, DTD 585 from one manufacturer may not dissolve in the electrolyte solution suitable for DTD 585 from another manufacturer.)	mm	Electrolyte solution will accept 33 % (volume fraction) to 50 % (volume fraction) Skydrol.
	nn	
	oo	Will accept 50 % (volume fraction) volume of oil (MIL 5606 B, MIL 7808 E and DTD 585).
	pp, qq	
	rr, ss	
	tt	For MIL 5606.
	uu	For lube oil.
	vv	
	zz	
Orange extract	a, b	
Paint (oil based)	gg, zz	
Particles captured by membrane filters (cellulose nitrate)	ff	Dissolve the membrane in 30 % (volume fraction) dimethylformamide in acetone before adding an equal volume of electrolyte solution. The electrolyte solution and solvent mixture should be filtered and stored separately. Ideal for particles in oil: filter the known volume of oil through membrane, then wash through with filtered petrol, carbon tetrachloride, trichloroethylene, etc. and dry the filter before dissolving. Extra dimethylformamide increases membrane solubility.
	gg, hh, ii, jj	
Paper pulp	a, b	
Peanut butter	m	
Penicillin	a satd.	
Phenacetin	a satd.	
Phenothiazine	a satd.	
Phosphors	a, b, e	Size range approximately 1 μm to 40 μm.
Photographic emulsions	a, i	40 g/l potassium nitrate solution may also be used.
Pigments	e, a, b	
Plaster of Paris	l, k	Electrolyte solution should be anhydrous.
Plastics	a, b, e	
Plating solutions	–	Analysed with no added electrolyte or diluted with

Material	Electrolyte solutions (see A.1)	Comments
		filtered distilled water.
Pollens	a, b	
Polyethylene	a, b	
Polypropylene	a, b	
Polystyrene	a, b	
Poly(styrene divinyl benzene)	a, b, e	Useful for calibration of orifices with most organic electrolytes.
Polytetrafluoroethylene	a	Almost any electrolyte solution is suitable. For finer powders, use alcohols or ketones to ensure thorough wetting.
Polyvinyl acetate	a	
Polyvinyl chloride	a, b	
Polyvinyl propylodone	a	
Polyvinyl toluene	a, b	
Porcelain	e	
Potassium chloride	l	
Potassium sulfate	l	
Potato starch	a	
Powdered milk	m	For fraction insoluble in alcohol.
	a	For fraction insoluble in water. Disperse in a few drops of 200 g/l sodium hydroxide solution.
Quartz	e	
Raney nickel in xylene	l, m	Slow reaction with m.
River sediment	–	See sediment.
River water	a, b	
	e	If no calcium salts are present.
Rouge	a	
Rust in gasoline	e	Filter out and resuspend in electrolyte solution.
Rutile	e	
Sand	a, b, e	
Sediment	a, b, e	
Shale	e	
Silica	e	
Silica gel	l	
Silicates	e	

Material	Electrolyte solutions (see A.1)	Comments
Silicon carbide	a, b, e	
Silicon nitride	m	
Silver halide	ww	
	a	For silver bromide.
Silver oxide	a, g	
Slag (basic)	a, e	
Sodium (metal)	–	Dispersions are usually in oil or grease, and electrolyte solutions made from ammonium thiocyanate and alcohols or ketones are suitable (see oils). Coupling agents, e.g. 1,1,2, trichloroethane, may be needed.
Sodium hydrogen carbonate	m	
Sodium chloride	m satd.	
Sodium hydroxide	xx satd.	Still not fully stable; use multi-channel models.
Soya flour	m, b	
Spironolactone	a, b	
Starch	a, e, l, m	Aqueous electrolytes suitable for hydrated form only.
Stearates	a, l	Difficult to wet. Spatulate with alcohol and use ultrasonics.
Steel	a(+G), f(+G)	
Sugar	m satd.	
Sulfadimidine	a satd.	
Sulfur	a, e	Wet by spatulation with alcohol before diluting with electrolyte solution.
Superphosphate (of lime)	m	
Talc	e	
Tantalum	a(+G), e(+G), f(+G)	
Tin	a(+G), f(+G)	
Tin oxide	e	Disperse in 50 g/l Calgon solution.
Titanium dioxide	e	
Tomato juice	a	
Toner, xerographic	a	
Tungsten	a, e(+G/S), f(+G)	
Tungsten carbide	e(+G), a(+G)	Can cold-sinter within hours of milling to cause permanent agglomeration.
Uranium	e(+G), f(+G)	
Uranium dioxide	e, c	Can cold-sinter (see tungsten carbide).

Material	Electrolyte solutions (see A.1)	Comments
Viscose	c	Or dilute with filtered distilled water.
Water, contaminants in	a	Dilute as required into electrolyte solution.
Whiting	l, m, a satd.	See calcium carbonate.
Wool fibre	m	
Yeast	a	
Yttrium iron garnet	e(+G)	Magnetic and needs frequent redispersing by ultrasonics.
Zeolite	–	See clay.
Zinc	yy	10 g/l Aerosol O.T. dispersant.
Zinc cadmium sulfide	e	Range usually 1 μm to 15 μm.
Zinc oxide	l, a, e satd.	Slightly soluble in water.
Zinc stearate	l	See calcium stearate.
	a, b, e	Wet.
	h, j	
Zinc sulfide	l	Not very suitable as the sulfide slowly oxidises to sulfate.
Zirconium oxide	a	Wet with 40 g/l sodium pyrophosphate solution.

Annex B
(informative)

Technique using two (or more) sensors

B.1 General

When it is necessary to use more than one orifice sensor to obtain a complete analysis, it is necessary to divide the suspension into two or more fractions at a suitable particle size which can be measured by each orifice. This is usually accomplished by wet sieving.

B.2 Separation

After analysis with the larger sensor, the beaker and the remaining suspension are weighed and the suspension passed through an electroformed or monofilament sieve with apertures equal to approximately half the diameter of the smaller orifice. The filtrate is collected in a clean, weighed, beaker. The first beaker is washed out on to the sieve with fresh electrolyte solution and the sieve itself is similarly washed. All the washings are collected in the second beaker. The dilution factor is calculated from the masses of the original and final suspensions.

B.3 Calibration

Suitable combinations of orifices similar to those in the Table B.1 are selected. The ratio of the diameters should not exceed 5:1, to ensure that the overlapping regions will match.

An electrolyte concentration is chosen such that the solution has a resistance low enough for use with the small orifice. For example, 10 g/l to 60 g/l sodium chloride solution is suitable for most orifice sizes. The electrolyte solution is prepared as recommended (see 6.6).

Both orifices are calibrated using the microsphere method (see 6.11.2) with the same calibration material. This will ensure that the size ranges in the overlap region will coincide.

Table B.1 — Suitable orifice diameter combinations

Particle diameter range (approx.) μm	Sensor diameter combination μm
0,6 to 84	30/140
1,0 to 120	50/200
1,4 to 168	70/280
2,8 to 240	140/400
0,6 to 240	30/140/400

B.4 Analysis

Each fraction is analysed with the respective orifice and the analyses are combined, allowing for the different dilutions. Full operational details or on-board computer programs are available from the instrument manufacturers, but the basic method is illustrated as follows.

Obtain the particle size distribution results from the larger aperture, as coincidence-corrected cumulative numbers of oversize particles (N) versus equivalent particle diameter (x) per unit volume of original suspension, and present, for example on log-log axes, the size distribution denoted by the points 1 to 9 in Figure B.1. After correcting for coincidence and any dilution, present the results from the smaller aperture in a similar way, for example as the points a to g in Figure B.1.

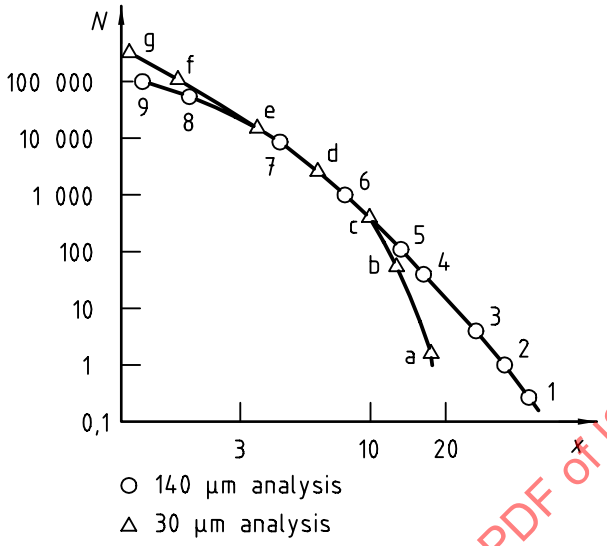


Figure B.1 — Illustration of the procedure for the overlap of distributions from two orifices

If the dilution factor is not known, the exact data for the smaller orifice should be multiplied by the factor which produces overlapping agreement with the central portion of the larger orifice data, as in Figure B.1.

The full size distribution will then be represented in this example by the points 1, 2, 3, 4, 5, 6, 7, e, f, g, or the points 1, 2, 3, 4, 5, 6, d, e, f, g; from which a cumulative mass or volume (weight) percentage distribution may be calculated by normal methods. In the overlap region the counts should agree to within 10 %.