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Particulate materials — Sampling and sample splitting for the determination of particulate properties

Matériaux particulaires — Échantillonnage et division des échantillons pour la caractérisation des propriétés particulaires

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Contents

Foreword

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The main task of technical committees is to prepare International Standards. 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.

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ISO 14488 was prepared by Technical Committee ISO/TC 24, *Sieves, sieving and other sizing methods*, Subcommittee SC 4, *Sizing by methods other than sieving*.

Introduction

The characterization of particle properties like size, form and specific surface area requires very careful sampling and sample splitting practices to be followed. The distributions of the values of such properties are related to the number of particles, which cannot be increased as in sampling for chemical analysis. Deviations from statistical values occur due to the presence of particles of different sizes and shapes for each component in a powder obtained from a sampled mass of powder.

Particulate materials — Sampling and sample splitting for the determination of particulate properties

1 Scope

This International Standard specifies methods for obtaining a test sample from a defined bulk of particulate material (powder, paste, suspension or dust) that can be considered to be representative of that bulk with a defined confidence level. It is particularly relevant to the measurement of particle size, size distribution and surface area.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3165, *Sampling of chemical products for industrial use — Safety in sampling*

ISO 6206, *Chemical products for industrial use — Sampling — Vocabulary*

ISO 9276-2, *Representation of results of particle size analysis — Part 2: Calculation of average particle sizes/diameters and moments from particle size distributions*

ISO 14887, *Sample preparation — Dispersing procedures for powders in liquids*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 6206 and the following apply.

3.1
bias
systematic difference between true (or accepted) value and measured value

3.2
"critical" size class
specific size class, whose sampling error, in its fractional mass, has a significant influence upon the product properties

3.3
error
difference between a measured value and the true value, which may have a random or a systematic nature

3.4
gross sample
primary sample, composed of several sample increments

3.5
grab sample
sample that has not been taken under well-defined conditions

3.6
primary sample
sample (single or composed) taken from a defined bulk product

3.7
representative sample
sample that has the same properties as a defined batch of material and represents the bulk material, within a defined confidence limit

3.8
sample
part of a defined bulk product taken for the purpose of characterization

3.9
sample increment
single sample, taken from any of a defined set of locations in a bulk product or at any of a defined set of times from a production/transportation line, to be mixed with other increments to form a gross sample

3.10
sampling sequence
sequence of sampling, sample division and combination steps that result in a test sample for a defined bulk product

3.11
spot sample
sample, taken at a defined location or production time, from a batch of material

3.12
test sample
sample that is entirely used for a property characterization

4 Abbreviations and symbols

For the purposes of this document, the following abbreviations and symbols apply.

CV	coefficient of variation, i.e. standard deviation relative to the corresponding mean value, expressed as fraction or percentage
F_{ϕ_1,ϕ_2}	standard F-distribution value with ϕ_1 and ϕ_2 degrees of freedom
FE	fundamental error
MMD	mass median diameter
n	total number of particles in sample or sample increment
n_0	number of particles in a defined size class
n_{min}	number of particles in a sample or sample increment required to obtain a defined maximum deviation ε_{max} with a defined level of confidence
n_{MMD}	required number of particles in a sample to meet the stated error of the MMD
n_r	total number of particles in the log-normal particle size distribution required to reach a maximum coefficient of variation of 3,16 % in x_{90}
N	number of measured samples
N_r	number of samples required to obtain a defined maximum deviation ε_{max}, with a defined level of confidence, between the estimated and the true mean value of a property of interest

$Q_0(x_i)$	cumulative number-based particle size distribution
$Q_3(x_i)$	cumulative volume- or mass-based particle size distribution
r	dimensionality (type of quantity) of a distribution: $r = 0$: number; $r = 1$: length; $r = 2$: area; $r = 3$: volume or mass
SD	standard deviation
s_y	estimate of standard deviation of y, coming from measurements
t	Student's t-factor for statistical significance, which depends on the confidence level taken and the number of degrees of freedom $(N - 1)$ (to be taken from statistical tables)
Var	variance
x	particle size
x_5	5 percentile size of the particles
x_{95}	95 percentile size of the particles
x_i	particle size corresponding to percentile i
y	value of any property of interest of the particulate material, e.g. specific size, shape, surface area
$\bar{y}$	mean value of y
z_c	critical z-value related to a defined confidence level according to the standard normal distribution (to be taken from statistical tables)
ε_max	defined maximum level of deviation at defined confidence level (half-width of the stated confidence interval)
γ	granulometric factor, related to the width of the particle size distribution, expressed by the ratio x_{95}/x_5 of the undersize particle size distribution; $\gamma \approx 0{,}25$ for wide particle size distribution with $x_{95}/x_5 > 4$; $\gamma \approx 0{,}5$ for $2 < x_{95}/x_5 < 4$; $\gamma \approx 0{,}75$ for $1 < x_{95}/x_5 < 2$; and $\gamma \approx 1$ for $x_{95}/x_5 \approx 1$
ρ	density of particles in kg/m^3
σ	standard deviation; square root of variance (theoretical value)
σ_g	geometric standard deviation of the log-normal particle size distribution
σ_P	fundamental error (standard deviation) of mass fraction of particles smaller than or equal to x_i, i.e. $Q_3(x_i)$

5 Principles of sampling and sample splitting

5.1 General

Particulate materials consist of discrete particles, each having its own properties such as size, shape, surface area, density and/or composition. Sometimes, the material is well mixed and the properties show only random variations with respect to location in the bulk and/or time of production. More often, however, segregation occurs due to the free-flowing behaviour of the material and/or fluctuations in the production process. This can result in a systematic deviation between the mean properties at different locations and at different times. For representative sampling, each of the particles in a bulk product must have the same probability of being sampled, in their proportions. For well-mixed materials, a single sample of adequate quantity may suffice. For most materials, some degree of segregation is to be expected. Then, several sample increments must be taken from different locations or at different production times. These are either analysed as such or combined into one primary sample. In most cases, there is no recipe for representative sampling. The quality of the sampling procedure can only be assessed by measurement. Often, the primary sample collected in this way is too large for characterization of the required property. Then, sample splitting is necessary until the required quantity for the test is obtained.

The total error of sampling and sample splitting consists of two parts: the fundamental error and the segregation error.

The fundamental error is related to the discrete nature of particles given their different properties. It is a statistical error, related to the random variations of the properties with respect to location. It represents the lower limit of the total sampling error. This error depends on the amount (number, mass) of sample taken.

The segregation error is related to the degree of segregation, or the degree of “de-mixing” of particles according to their size, shape and density. It cannot be predicted, but only assessed by measurement of samples taken at different locations in the bulk and at different times of production. These measurements provide an estimation of the segregation error (see 5.3).

Given the complex behaviour of particulate materials, it is required that the complete procedure for sampling and sample splitting be described in a sampling plan (see Clause 6).

5.2 Fundamental error

5.2.1 Number distributions $Q_0(x)$

For number-based size distributions, the fundamental error [expressed as the variance Var or squared standard deviation σ of a fraction $Q_0(x_i)$ at any point x_i] can be calculated using the mathematics of binomial distributions [1], [6]:

$$\mathrm{Var}[Q_0(x_i)] = \sigma_{Q0,i}^2 = Q_0(x_i)[1 - Q_0(x_i)]/n \tag{1}$$

If the number of particles in a size class or above a certain size is very small in comparison to the total number of particles taken into account for a measurement, then Poisson statistics may be used for estimating the variance or the standard deviation:

$$\mathrm{Var}(n_0) = \sigma(n_0)^2 = n_0 \tag{2}$$

For example, for the number of particles larger than x_{90}, it can be seen that

$$n_0 = [1 - Q_0(x_{90})]n \tag{3}$$

and, since $Q_0(x_{90}) = 0{,}9$ or almost 1, Equations (1) and (3) give approximately the same answers.

If the fundamental error is the only error, the minimum number of particles n_{min} required to obtain a defined maximum deviation $\varepsilon_{\mathrm{max}}$ with a defined confidence can be derived from:

$$\varepsilon_{\mathrm{max}} = z_{\mathrm{c}}\sigma_{Q0,i} = z_{\mathrm{c}}\sqrt{Q_0(x_i)[1-Q_0(x_i)]/n_{\mathrm{min}}} \tag{4}$$

or

$$n_{\mathrm{min}} = \{Q_0(x_i)[1 - Q_0(x_i)]\}z_{\mathrm{c}}^2/\varepsilon_{\mathrm{max}}^2 \tag{5}$$

where z_{c} is the critical z-value related to the defined confidence level according to the standard normal distribution and may be obtained from statistical tables.

The standard deviation of x_i can be calculated from $\sigma_{Q0,i}$ through multiplication by the reciprocal value of the slope of the cumulative size distribution at point x_i:

$$\sigma_{xi} = \sigma_{Q0,i}\, \mathrm{d}x_i/\mathrm{d}Q_0(x_i) \tag{6}$$

The coefficient of variation of x_i can be calculated from this standard deviation by multiplication by 100 and division by x_i:

$$\mathrm{CV}_{xi} = 100\sigma_{xi}/x_i \tag{7}$$

5.2.2 Volume- or mass-based distributions $Q_3(x)$

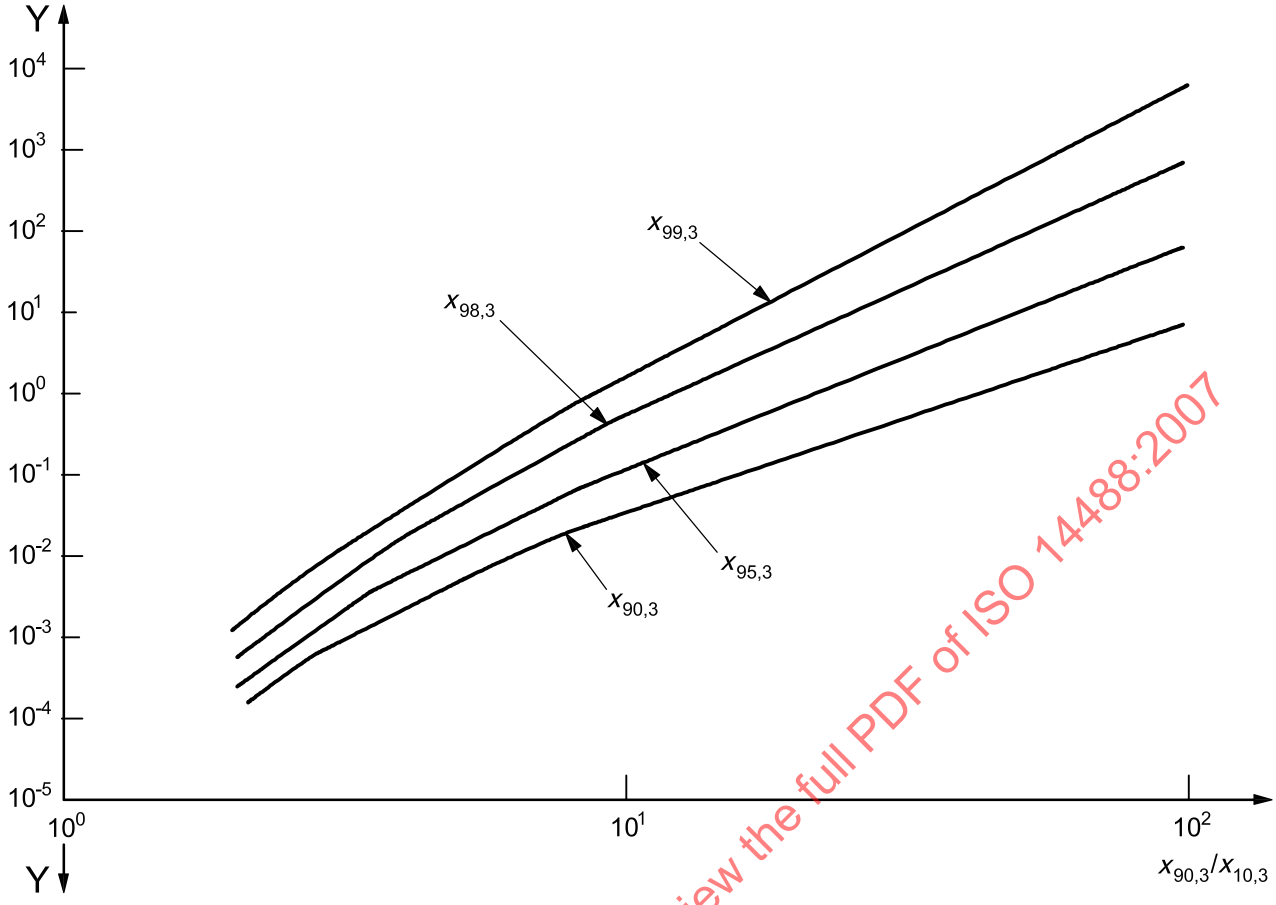
For volume- or mass-based size distributions, the general calculation of the fundamental error is not simple. One way is to use a spreadsheet programme (e.g. Excel) to convert the measured volume-based size distribution of a typical sample into the corresponding number distribution. The conversion principles and equations given in ISO 9276-2 shall be used.

This estimation of the minimum amount of sample in view of a stated minimum fundamental error shall always be the first step in a sampling procedure.

As an example of the results from such calculations, Figure 1 and Figure 2 are presented for a 1 % coefficient of variation in x for various characteristic sizes as log-normal size distributions. The calculations were conducted for distributions around a median size of 30 µm with a material density of 1 000 kg/m^3. A detailed calculation is given in Annex B.

Figure 1 shows that, for a constant percentile, the sample mass required to reach a coefficient of variation of 1 % increases with particle size distribution width. It increases from about 10 mg to 1 kg as the distribution width ratio ($x_{90,3}/x_{10,3}$) increases from 2 to 100. The sample mass required is also increased if the fundamental error is to be maintained for percentiles ever closer to the highest limit of the distribution ($x_{90,3}$, $x_{95,3}$, $x_{98,3}$ and $x_{99,3}$). For a distribution by mass, it should be noted that a 10 times higher mean particle size requires a 1 000 times higher sample mass and *vice versa*. Note also that acceptance of a 10 times larger coefficient of variation in the fundamental error requires 100 times less sample mass.

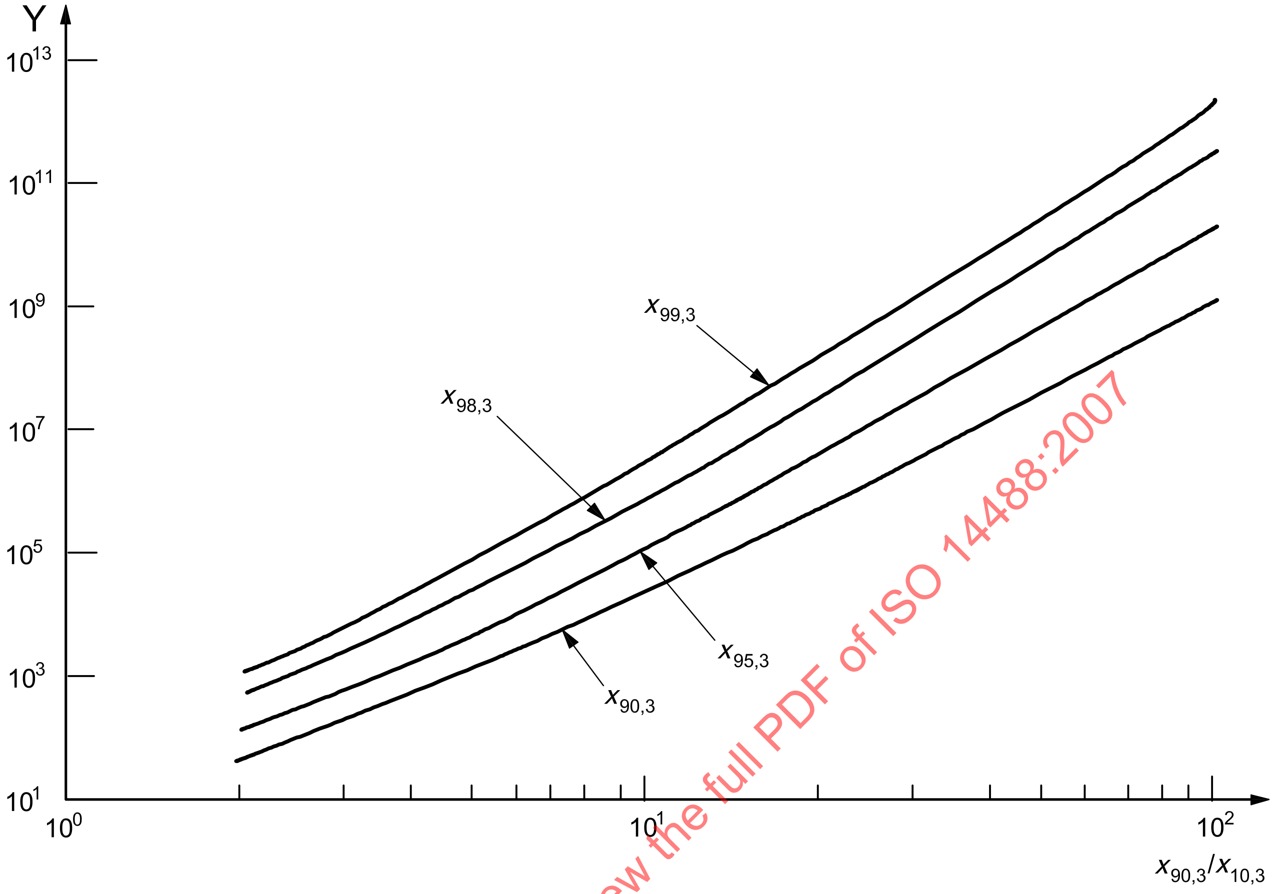
Figure 2 illustrates that, for larger distribution width ratios, larger numbers of particles must be counted to ensure a result whose error remains below the target of a 1 % coefficient of variation. For a very narrow size distribution, counting a few hundred particles is all that is required. However, for very broad distributions, a number in excess of 10 000 000 will need to be assessed and counted.



Key

Y minimum sample mass (g)

Figure 1 — Minimum sample mass for 1 % FE



Key

Y ratio of total number of particles to the number larger than the specified size

Figure 2 — Ratio of total to fractional particle number

5.3 Total error/number of samples or increments

It is to be expected that some degree of segregation will have occurred in the bulk product. The total sampling error shall be assessed through measurements of the property of interest in multiple samples. These samples shall have about the same size and come from different locations in the bulk or have been taken at different times during the production process. The minimum sample size shall be calculated as indicated in 5.2 and Annex B. From these multiple measurements of the value y of a property, both the mean value $\bar{y}$ and its standard deviation s_y may be calculated from

$$\bar{y} = \frac{1}{n}\sum y_i \tag{8}$$

and

$$s_y = \sqrt{\frac{\sum_i (\bar{y} - y_i)^2}{N-1}} \tag{9}$$

where N is the number of measured samples.

This total error may first be compared with the fundamental error as calculated above and the degree of segregation assessed. Secondly, it can be converted to a confidence interval indicating a maximum level of deviation ε_{max} at a given level of confidence using

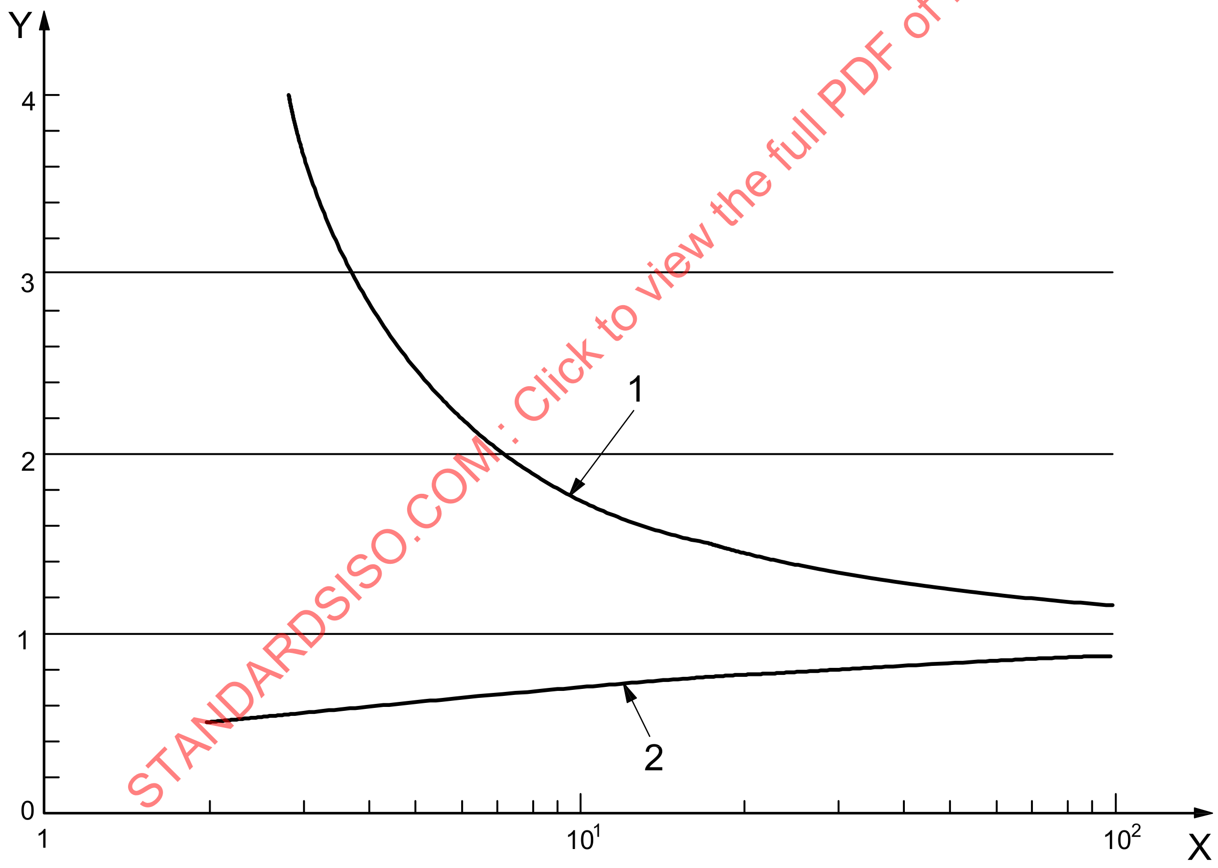
$$\varepsilon_{\text{max}} = ts_y / \sqrt{N} \tag{10}$$

where t is Student's t-factor for statistical significance, which may be obtained from statistical tables. The t-value is dependent upon the confidence level taken and the number of degrees of freedom ($N - 1$).

Equation (10) may be rearranged to calculate the number of samples (or sample increments) N_r required for a deviation ε_{max} at a defined level of confidence between the estimated and the true mean value of y:

$$N_r = (ts_y / \varepsilon_{\text{max}})^2 \tag{11}$$

When the measured values y of a property follow a normal Gaussian distribution, which is generally true, then the confidence interval of the variance of these measurements can be derived from a chi-squared distribution, which is not symmetrical. This is illustrated in Figure 3, which shows the 95 % confidence limits for the ratio of true standard deviation to calculated standard deviation as a function of the number of degrees of freedom.



Key

X number of degrees of freedom

Y ratio of true standard deviation to calculated standard deviation

1 upper limit

2 lower limit

Figure 3 — 95 % confidence limits for confidence interval of standard deviation

Figure 3 shows stabilization of this confidence interval when generally more than 30 samples are taken into account for a best estimate of precision.

When measuring particle size and surface area, the exercise of estimating the standard deviation of the mean measured property is only performed at the beginning, when starting with a given bulk product or production process, or during validation. When products are to be checked on a regular basis, the minimum number of samples required to assess the product quality may be taken as sample increments. These sample increments may be combined to create a gross sample if they have the same mass. Such a gross sample may be too large for characterization and thus has to be subdivided to obtain the required quantity of test sample. During subdivision (sample splitting), the same equations can be applied as indicated earlier in this clause.

6 Sampling plan

A sampling plan shall be specified and documented. If a quality standard of the ISO 9000 series is used, the sampling plan shall be a part of the quality standard documentation (see Reference [11]).

The sampling plan shall consist of a general part and a technical part.

It is recommended, but not mandatory, that the sampling plan be made for the whole sampling sequence from primary sampling to the final test portion(s).

The general part shall address at least the following aspects:

- Material description.
- All known relevant information on the powder to be measured (for example, variance, hygroscopicity, reactivity, cohesion, etc.).
- All known hazards related to the powder (for example, toxicity, flammability).
- Description of the task.
- The use of the information to be estimated from the powder (for example, sales contract, internal quality measurement).
- The random variables to be estimated in exact terms (for example, mean percentage of material finer than 10 µm in production batch).
- The variance (coefficient of variation) and the related limit of confidence shall be specified for all sample splitting stages. The total sample splitting variance estimate shall also be computed.

The technical part shall address at least the following aspects:

- Physical appearance of powder at sampling point(s).
- Sampling sites for all sampling and sample splitting stages, including site requirements.
- Method of primary sampling (if applicable) (random, systematic, stratified, staged, sequential).
- Mode of increment withdrawal (continuous, discrete).
- Type of increment (time, mass, number).
- Size of increments (number of particles or mass) in sampling and sample splitting stages.
- Number of increments to be taken in primary sampling and subsequent sample splitting stages.

- Number of increments to be chosen for further sample splitting in each stage.
- Combination of increments (if applicable).
- Required reduction ratios for all sample splitting stages and overall reduction ratio for test sample.
- Method(s) of sample splitting (one or more stages).
- Detailed description of all other sample handling procedures used (i.e. mixing, sonification, dispersant additions, etc.).
- Method of final analysis.
- Number of measurement repetitions for each test sample.
- All equipment needed for sampling and sample splitting stages.
- Cleaning procedures for all equipment and sample containers.
- Qualifications of personnel for each stage of the sampling sequence.
- Sample marking.
- Sample storage procedure(s) and place(s).

All equipment and methods shall be validated and such documents shall be a part of the sampling plan. The requirements specified in Clause 7 shall be applied.

7 General procedures

7.1 Safety precautions

Safety precautions are necessary when sampling and handling hazardous materials. Relevant statutory requirements shall be followed and reference shall be made in the sampling plan to any toxicological data, precautionary measures to protect the operator and remedial measures in the event of an accident. Measures described in ISO 3165 shall be taken into consideration.

7.2 Primary sampling

Representative sampling from a bulk particulate product requires that all particles have equal probability of being taken into the sample, in their given proportions. Sample increments of about the same size shall be taken from as many locations in the bulk product as practical and combined into a single gross sample. These locations shall be chosen carefully and be described in the sampling plan. In order to minimize errors due to segregation, this sampling shall be done at a place where segregation is minimal. Sampling from a moving stream is a preferred method. Some general rules for designing sampling equipment are as follows:

- The preferred design is one which collects the sample over the whole particulate stream for part of the time and not a fixed part of the stream continuously.
- The frequency of sampling shall differ from that of any major process fluctuations or loading sequences. If the frequency of such fluctuations is unknown, further investigations are necessary (see e.g. References [2] and [8]).
- The sampler and sample container shall have no constraints, so that even the largest particles are easily accepted. Thus, the diameter of sampling tubes and the distance between cutter edges shall be at least three times the size of the largest particle and not be smaller than 10 mm. However, for liquid dispersions of small particles, a minimum size of 2 mm is acceptable.

- The sample container shall have sufficient volume to easily receive the full sample.
- Samplers shall have thin walls or sharp edges to promote good control of acceptance of particles based on their centre of gravity.
- The speed of a sample cutter or sample tube shall be sufficiently low in order to avoid large particles being lost by collision with the sides of the cutter or tube and small particles being carried away in the upward air stream. As a rule of thumb, cutter speed shall be lower than 40 cm/s.
- Local sampling tubes in pipelines shall be iso-axial to the pipe.
- Local sampling in pipelines shall be done iso-kinetically where possible, while keeping the linear flow rate about the same. The flow in the pipeline shall be either undisturbed or mixed thoroughly. No intermediate flow regimes shall be used.

WARNING — Manual sampling from heaps always leads, with segregating materials, to large sampling errors.

7.3 Sample handling

Sample increments shall be entirely utilized at all stages of sample division, preparation and measurement. No material may be added to or taken from the increment. Incomplete or contaminated increments shall not be used.

Throughout all the procedures and stages, the sample shall be protected from any contamination by foreign particles.

Samples shall not be unduly transported or handled. If transportation cannot be avoided, however, the method of transportation shall be agreed upon between the parties concerned. Transportation and handling shall be validated to ensure that changes in the particle properties of interest do not occur.

Any sample handling procedures, such as homogenization by mixing, thermal drying or dispersion by sonication or other methods, shall be validated to ensure that changes in the particle properties of interest do not occur.

Appropriate and validated thermal drying conditions (heat source, temperature, atmosphere, ventilation, etc.) shall be specified. After thermal drying, the material shall be allowed to cool in a desiccator. If the material is hygroscopic, it shall also be stored in a desiccator.

Appropriate and validated dispersion conditions shall be specified.

Samples shall be stored so that no alteration in the properties of interest takes place. They shall be stored away from direct daylight and shall not be subject to large temperature changes. Longer periods of storage shall be validated.

Any equipment needed in the process of sampling shall be thoroughly cleaned.

7.4 Sample containers

Storage containers used for storing any sample shall be capable of holding the entire quantity of the sample. The storage container shall be clean and sufficiently robust. The storage container shall either have a lid to close it securely or be of such a construction that it can be closed tightly in another way.

7.5 Marking of sample containers

Containers shall be marked if the divided sample is not going to be used immediately. The container markings shall include the following information:

- sample identification:
  - number,
  - in the case of parallel samples, the total number of samples and the sequence number within the total;
- sampling level identification;
- name of commodity;
- identification of lot number and producer's name;
- date of sample preparation;
- name of person who carried out the sample preparation and the affiliation;
- other necessary information (if applicable):
  - carrier fluid identification,
  - any dispersion and stabilization reagents employed,
  - other treatments to which the sample has been subjected,
  - special properties of the material, such as hygroscopicity, segregation tendency,
  - information concerning safety,
  - identification of the sampling plan applied.

An alternate strategy is to mark the sample containers with a sample identification number which can be related to the above information recorded in a sample preparation laboratory book or computer file. Computer files shall have a backup.

In the event of further division of a stored sample, the original sample identification shall be recorded on the containers containing the newly divided samples.

Markings on sample containers shall be made in such a way that they will not become illegible during the storage period.

8 Sample division techniques

8.1 General

Often the size of primary samples is too large for property characterization purposes. In such cases, the sample shall be divided to give a test sample of a suitable size. Several techniques exist for sample splitting. Their applicability depends on the flow properties and the homogeneity of the primary sample from which a representative test sample is desired. Sometimes, different techniques are used in combination.

8.2 Spinning riffler

Spinning rifflers (rotary samplers) are the best choice to sub-sample free-flowing particulate materials. Other materials may be made to flow freely by the use of additional agents in known quantities. Sticky and strongly agglomerated powders are excluded. Spinning rifflers are available in different sizes; they can provide samples ranging from about 0,5 g to 300 g.

The spinning riffler consists of a feed hopper, a vibratory feeder and a turntable or other rotating divider ring where the sample holders are located.

Before sample splitting, the sampler shall be clean. The hopper design shall be such that a constant, non-segregating, even mass flow of sampled material is ensured. The sample holders shall be designed in such a way that no material to be sampled is lost outside the sample holders or remains trapped within the hopper, vibratory feeder, divider ring or any other part of the sampler. Special care shall be taken in the riffler design and its operation that material will not be retained between the sample holders. The material shall be carefully mixed before being placed in the feed hopper. The vibratory feeder is then actuated and left to operate until the entire sample has been divided. The hopper and the vibratory feeder shall be cleaned while the riffler is still running so that no material remains in the hopper or in the vibratory feeder.

8.3 Static riffle divider

Static rifflers — table rifflers or chute rifflers — are capable of providing large quantities of samples for materials that are free-flowing or can be made to flow evenly. Their quality of division is generally worse than that of spinning rifflers. They usually find application with very coarse materials. They shall not be used for materials that readily liberate dust, nor for friable materials.

The material shall be carefully mixed in a feed container and poured uniformly into the divider to divide the sample into parts. Any one of the divided parts shall be selected randomly as the divided sample. Care shall be taken to prevent clogging of the riffles. If clogging does occur, the whole sample shall be re-mixed and a new pour carried out after cleaning the riffler.

Slow pouring of sample into the riffler shall be avoided.

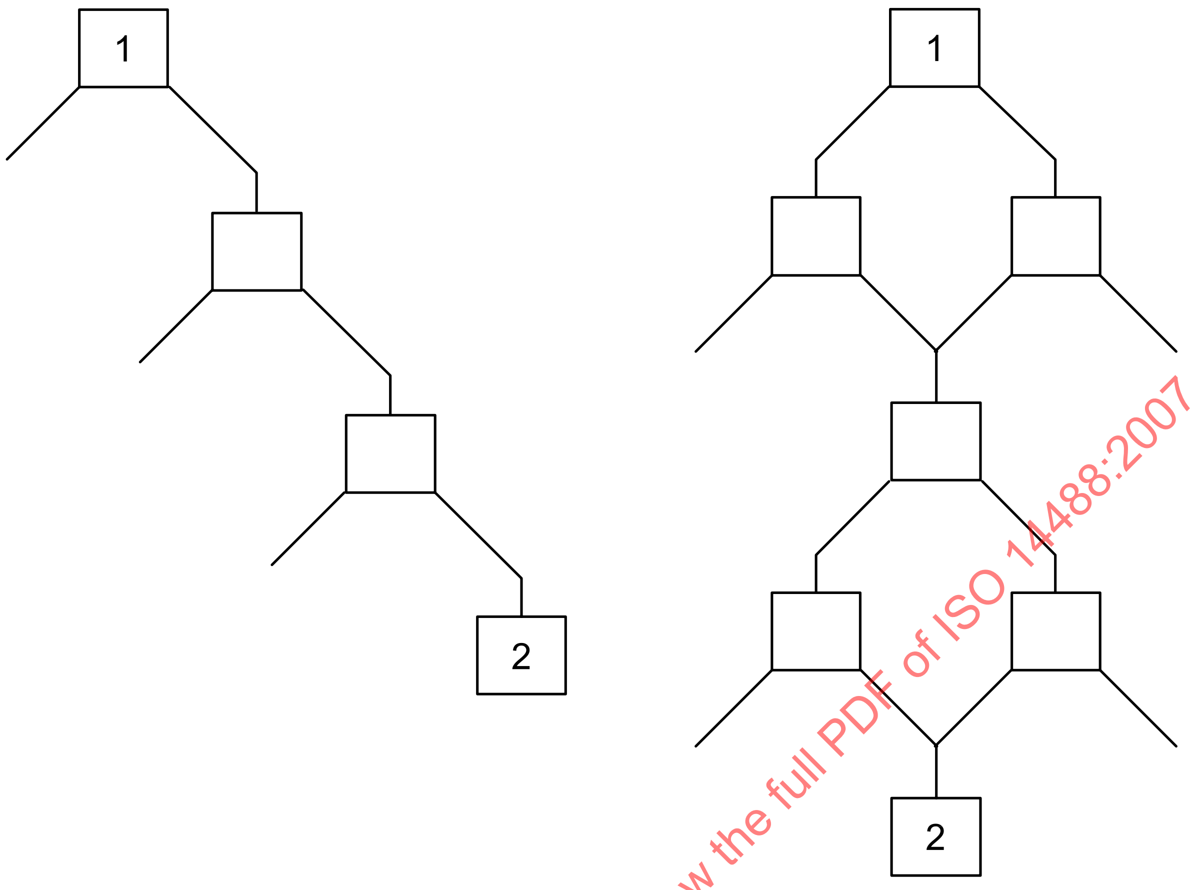
The size of the riffle divider shall be in accordance with Table 1.

Table 1 — Size of static riffler to be used

Maximum particle size mm	**Opening width** mm
20 to 16	50
16 to 10	30
10 to 5	20
5 to 2,5	10
below 2,5	6

The static riffler shall be used in accordance with one of the two methods illustrated in Figure 4.

In method 1, the sample is divided into two parts. One of these parts is further divided into two, and so on, until the sample size required for final analysis is obtained. The reduction ratio for division into l stages is $\frac{1}{2^l}$.



a) **Method 1**

b) **Method 2**

Key

1 sample to be divided

2 divided sample

Figure 4 — Pouring schemes for a riffler

In method 2, the sample is divided into two parts and both parts are separately divided into two. Two of the halves produced by this division are combined and the resulting combined sample then divided again in the same two-step mode.

The reduction ratio is $\frac{1}{2^{l/3}}$.

Method 2 is the preferred method.

8.4 Coning and quartering

8.4.1 General

The technique of coning and quartering can be applied successfully for powders with poor flow properties. Due to the manual operations involved, the technique tends to be operator sensitive.

8.4.2 Coning and quartering of powder

The material to be coned and quartered shall be thoroughly mixed in a mixing container. The material is then poured carefully on to a hard, clean, nonporous surface. The pouring shall be made in a single pass and the pouring point (spatial location) shall not be moved from the centreline of the cone which forms during the pour.

For quartering, a knife with four crossed blades is used. The height of each blade shall be more than the height of the sample cone formed by pouring. The knife is carefully inserted into the top of the sample. The movement of the blade shall follow the centreline of the sample cone. Care shall be taken that the knife is inserted right to the bottom of the cone. A randomly chosen quarter is then removed as a sample without moving the knife. All the particles shall be removed, using a small brush if necessary.

This method shall not be used for powders having a tendency to segregate due to large differences in density or in particle size, or for powders that are prone to dust liberation. The method shall not be used for hazardous materials.

WARNING — This method tends to give a high random error and is operator sensitive. It may also give systematic errors. It shall be validated before use.

8.4.3 Coning and quartering of a paste

When using the coning and quartering method for pastes, form the material into a cone shape. A conical mould in two halves may be used. Otherwise, the procedure is similar to the coning and quartering of dry powders.

Direct quartering of a filter cake shall not be carried out.

8.5 Increment division method

The increment division method can be used not only for materials with good flow properties but also for those with poor flow properties. Here, too, the quality of sample division depends upon the ability of the operator.

The material shall first be mixed thoroughly without dust formation. The material is then spread on a flat, clean surface and formed into a rectangular bed having a uniform thickness as given in Table 2. Mark the rectangle into areas of equal size, the number of areas corresponding to the number of increments required. Take a sample from each area, selecting the sampling point within the area randomly. Before sampling, insert a plate, against which the sample will be taken, from the top to the bottom of the powder layer. Then, insert a sampling shovel into the sample layer down to the bottom of the layer. Use a blunt-ended shovel with sidewalls. Take the sample in a direction perpendicular to the inserted plate, advancing the shovel until it makes contact with the plate. When removing the shovel from the sample bed, remove the plate and shovel together to ensure that no material is lost. Combine the sub-samples thus obtained to give a combined sample.

Table 2 — Bed thickness in manual incremental division of sample

Maximum particle size mm	**Thickness of sample layer** mm
20	35 to 60
16	30 to 45
8	25 to 35
4	20 to 30
2	15 to 25
1	10 to 15
0,5 or finer	5 to 10

If a different quantity of sample is needed than that obtained by the above procedure, either the size of the increment or the number of increments shall be varied. By weighing the first sub-sample obtained, an estimate of the size of the final combined sample can be computed. If adjustments are necessary, the sub-sample already taken is returned to the original material and the procedure is re-started with a new increment size or number of increments.

This method shall not be used for powders having a tendency to segregate. Nor shall it be used for materials that show a large variation in particle density or size or for materials that are prone to dust liberation. The method shall not be used for hazardous materials.

WARNING — This method tends to give a high random error and is operator sensitive. It may also give systematic errors. The method shall be validated before use.

8.6 Scoop sampling

Scoop sampling is, in general, subject to large errors. Only for well-mixed, sticky powders having a fairly narrow particle size distribution, or for pastes, might it provide adequate quality. The technique tends to be very operator sensitive due to the manual nature of the operations involved.

Before sampling, the particulate material shall be mixed well within its container by stirring or rotation. Free-flowing materials shall be mixed with a few drops of liquid, containing some dispersant [1], to form a paste (see 8.7). Several sample increments, preferably at least ten, shall be taken by means of a scoop, spoon or spatula and combined to form the test sample.

8.7 Sampling from paste

This method allows extraction of very small samples from pastes and powders after they have been mixed into a (homogeneous) paste. In a paste, the high concentration of solids in the liquid restricts segregation of particles.

Small spot samples to be used as test portions may be obtained from a well-mixed paste made of fine powder.

Prior to preparing the paste, prepare a dispersing liquid containing suitable amounts of dispersants. Care shall be taken that the dispersing liquid contains no dispersant particles that may interfere with the measurement. Place a weighed amount of solids onto a clock glass. Add a few drops of the prepared dispersing liquid and carefully knead the powder to a paste. The total amount of liquid shall be such that the material is barely in paste form. Care shall therefore be taken in adding the final drops of dispersing liquid. After the paste has formed, it shall be thoroughly mixed.

Samples may be taken from the paste either at random or systematically. In systematic sampling, the surface of the paste is divided into parts and a sample taken from each part.

This method shall be validated by comparing it with another sample splitting method to confirm that no particle breakage or dissolution occurs.

8.8 Suspension sampling

8.8.1 General

Suspension sampling allows preparation of very small samples (10 cm^3 or less) from suspensions and also from powders after they have been mixed with a dispersant to give a homogeneous suspension. The suspension shall, of course, be stable (no sedimentation) during the period of sampling.

8.8.2 Sample splitting by pipette

With powders, prepare the suspension by filling a cylindrical vessel with liquid containing a suitable amount of dispersant and add the sub-sample prepared by any of the methods described earlier. Dispersing procedures shall be in accordance with ISO 14887. Take care that the powder is properly wetted and ensure that no solids are left on the walls of the vessel. The vessel shall be equipped with a stirrer and with baffles to prevent symmetrical flow during mixing. Agitate the suspension thoroughly and, while agitating, withdraw aliquots containing the required test portion amounts using a pipette or dropping tube of an appropriate volume and orifice diameter.

After sampling, flush the pipette with particle-free suspension liquid and add this liquid to the sample aliquot taken.

Before reinserting the pipette in the suspension, clean the outside of the pipette.

This method is best suited for powders with a maximum particle size of about 20 µm to 40 µm. It is not well suited for powders having a large variation in particle density, shape or size.

WARNING — This method may cause systematically low contents of coarse particles if used for powders containing coarse and/or dense particles.

The method shall be validated for all new materials.

8.8.3 Sample splitting using multiple capillary tubes

Multiple suspension samples may be obtained simultaneously by permitting a dispersed sample to flow through a set of capillary tubes spaced symmetrically in a vessel. Typically, the capillary tubes have a bore of 0,7 mm. The sampling process may be validated by measuring the volume of particle-free suspension liquid which comes through each capillary. The volume delevered by the capillaries to the sample receivers shall be accurate to within 2 %.

Check that the suspension sampler is clean. Test the sampler, both before and after the sample splitting operation, for blocked capillary tubes. To do this, add particle-free suspension liquid to the sampler and observe the flow of liquid from the capillaries while applying an overpressure to the sampler. If any blockage is observed, clean the blocked capillaries and repeat the check.

It is recommended that the sampler not be used for powders whose maximum particle size exceeds about one-third of the capillary tube bore.

Prepare a suitable amount (about 100 cm^3) of suspension in a separate container and pour it into a glass vessel of about 150 cm^3 which can be tightly sealed and is equipped with a stirrer and capillary tubes attached to its base plate. Wash out the container, adding the washing liquid to the suspension in the glass vessel. Make sure that the sample receivers can receive the whole of the prepared suspension plus all the washing liquid. Mix the suspension thoroughly for 15 s to 30 s. While mixing, apply a slight under-pressure to the sampler to keep the capillaries free of suspension. Place the capillary tubes in the sample receivers and, while continuing to stir the suspension, split the sample by applying an over-pressure to the sampler. When splitting is complete, thoroughly wash the sampler.

9 Validation

The quality of the primary sampling procedure shall be validated using the actual material and method adopted. The standard deviation and confidence interval shall be calculated using the procedures given in 5.3 and the maximum error at the given confidence level shall be compared with the required maximum error.

The quality of the sample splitting technique(s) shall also be validated.

The simplest validation to be performed when the dry riffler splitting technique is used is a mass validation. Measure the mass of the gross sample together with the masses of all the increments. Repeat this three times. If the mean loss of material is larger than 1 %, or if the loss in any single experiment is more than 1,3 %, the riffler is deemed to be not working properly and this shall be corrected before further use. If the coefficient of variation in the mass of the increments is larger than 1 %, then the riffler is also deemed to be not working properly.

For a more rigorous validation of the sample splitting method, the method given in Annex A can be used. The material to be split shall be a standard reference material that has a similar particle size distribution and similar flowability to the material to be treated.

The results shall be verified against the required total variance. The results can also be used to design the sample treatment chain.

Annex A

(informative)

Calculation of variances at different stages in the sampling sequence

A.1 General

The variances at the different stages in the sampling sequence can be estimated by an experimental method covering either the full sequence or part of the sequence.

A.2 Full sequence

In the full sequence, all sub-samples taken are further sampled or analysed. The symbols x_i, x_{ij}, x_{ijk} denote the experimental values of the random variable x at the different stages of sampling and size analysis (see Figure A.1). The notation $x_{ij\bullet}$ is used for the mean over k, $x_{i\bullet\bullet}$ is used for the mean over j and k, and $x_{\bullet\bullet\bullet}$ is used for the mean over i, j and k. The number of primary sample increments (stage denoted by ξ_i) is denoted by n_1, the number of secondary sub-samples (stage denoted by ψ_{ij}) is denoted n_2 and the number of size analyses (stage denoted by ζ_{ijk}) from each sub-sample is denoted by n_3. Using this notation, the sum of the squares of the measurements can be given as

$$\sum_{ijk}\left(x_{ijk}-x_{\bullet\bullet\bullet}\right)^2=\sum_{ijk}\left(x_{ijk}-x_{ij\bullet}\right)^2+n_3\sum_{ij}\left(x_{ij\bullet}-x_{i\bullet\bullet}\right)^2+n_2n_3\sum_{i}\left(x_{i\bullet\bullet}-x_{\bullet\bullet\bullet}\right)^2 \tag{A.1}$$

or, in a shorter notation,

$$\sum_{ijk}\left(x_{ijk}-x_{\bullet\bullet\bullet}\right)^2=s_0+s_1+s_2 \tag{A.2}$$

The sums of squares represent estimates of the variations in the different phases of the error hierarchy as given in Table A.1.

Table A.1 — The estimates that the sums of squares represent

Sum of squares	Number of degrees of freedom	Represents an estimate of
$s_0=\sum_{ijk}\left(x_{ijk}-x_{ij\bullet}\right)^2$	$n_1n_2(n_3-1)$	$n_1n_2(n_3-1)\sigma_0^2$
$s_1=n_3\sum_{ij}\left(x_{ij\bullet}-x_{i\bullet\bullet}\right)^2$	$n_1(n_2-1)$	$n_1(n_2-1)(n_3\sigma_1^2+\sigma_0^2)$
$s_2=n_2n_3\sum_{i}\left(x_{i\bullet\bullet}-x_{\bullet\bullet\bullet}\right)^2$	(n_1-1)	$(n_1-1)(n_2n_3\sigma_2^2+n_3\sigma_1^2\sigma_0^2)$

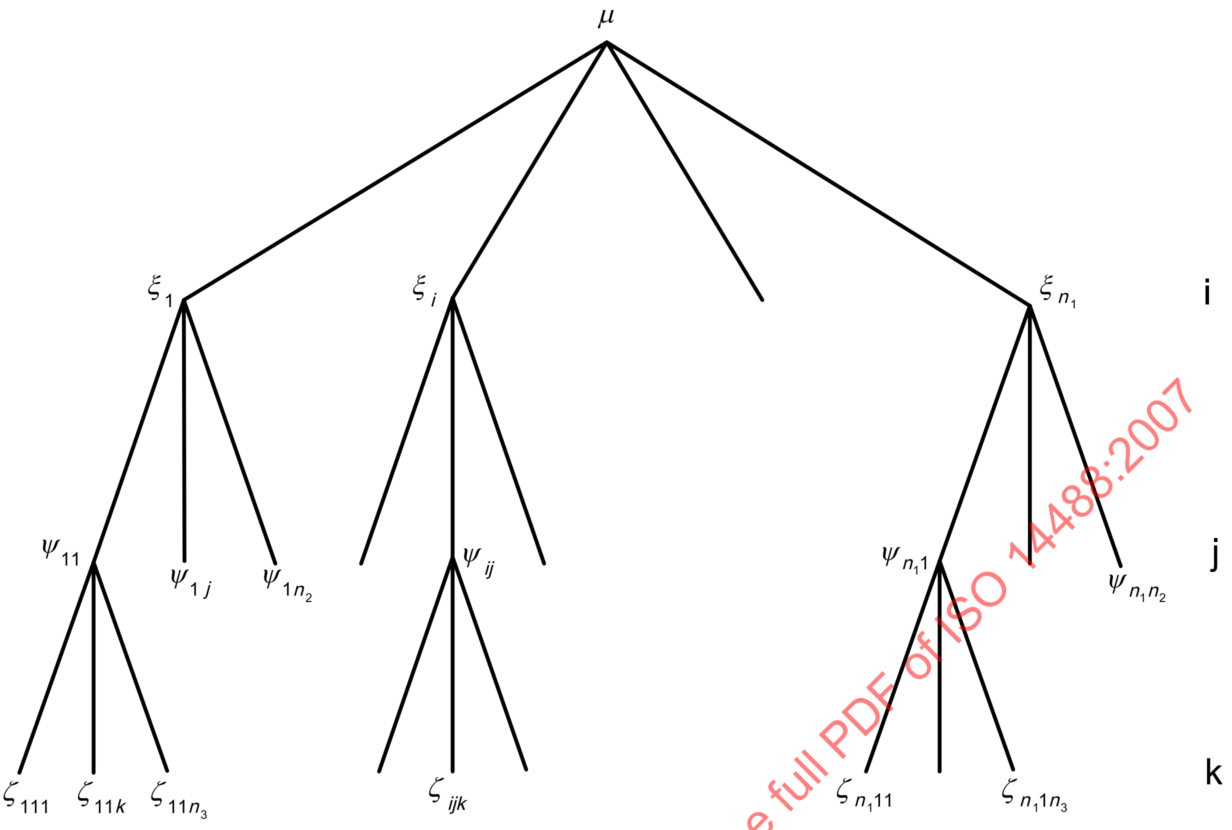


Figure A.1 — Sampling sequence errors
(for meanings of symbols, see Clause A.2)

Using Table A.1, we can obtain the equations used for testing the statistical significance of the variances of the different stages of sample preparation and division.

For the statistical assumption that $\sigma_1 = 0$, the test equation is

$$\frac{s_1/\left[n_1\left(n_2-1\right)\right]}{s_0/\left[n_1 n_2\left(n_3-1\right)\right]} = F_{\phi_1,\phi_2} = F_{\left[n_1(n_2-1)\right],\left[n_1 n_2(n_3-1)\right]} \qquad \text{(A.3)}$$

where F_{ϕ_1,ϕ_2} is the standard F-distribution value with ϕ_1 and ϕ_2 degrees of freedom.

In a similar manner, a test function can be formulated for the statistical assumption that $\sigma_2 = 0$; $\sigma_1 = 0$. If this assumption cannot be accepted, then

$$\frac{s_2/\left(n_1-1\right)}{s_1/\left[n_1\left(n_2-1\right)\right]} = F_{\phi_1,\phi_2} = F_{(n_1-1),\left[n_1(n_2-1)\right]} \qquad \text{(A.4)}$$

If the statistical assumption that $\sigma_2 = 0$; $\sigma_1 = 0$ can be accepted, the test function is

$$\frac{s_2/\left(n_1-1\right)}{\left(s_0+s_1\right)/\left[n_1\left(n_2 n_3-1\right)\right]} = F_{\phi_1,\phi_2} = F_{(n_1-1),\left[n_1(n_2 n_3-1)\right]} \qquad \text{(A.5)}$$

The latter equation should be used if the assumption of test function (A.3) is accepted.

If neither the assumption $\sigma_2 = 0$ nor the assumption $\sigma_1 = 0$ can be accepted, then estimates for the variances of different sample treatment tasks can be evaluated by solving the equations in Table A.1.

Variances should not be estimated if the estimates prove to be without significance.

A.3 Partial sequence

In the case of a partial sequence, only a selected number of sub-samples are treated further. Let the number of sample divisions be denoted as K_i for sampling stage i and the number of sub-samples taken be n_i for stage i.

The mean value $\bar{x}$ of the random variable x is then (see Figure A.2)

$$\bar{x} = \frac{1}{n_1 n_2 n_3} \sum_{i=1}^{n_1} \sum_{j=1}^{n_2} \sum_{k=1}^{n_3} x_{ijk} \tag{A.6}$$

The estimates for the variances for the stages are

$$s_3^2 = \frac{1}{n_1 n_2 \left(n_3 - 1\right)} \sum_{i=1}^{n_1} \sum_{j=1}^{n_2} \sum_{k=1}^{n_3} \left(x_{ijk} - x_{ij}\right)^2 \tag{A.7}$$

$$s_2^2 = \frac{1}{n_1 \left(n_2 - 1\right)} \sum_{i=1}^{n_1} \sum_{j=1}^{n_2} \left(x_{ij} - x_i\right)^2 - \frac{s_3^2}{n_3} \tag{A.8}$$

and

$$s_1^2 = \frac{1}{\left(n_1 - 1\right)} \sum_{i=1}^{n_1} \left(x_i - \bar{x}\right)^2 - \frac{s_2^2}{n_2} - \frac{s_3^2}{n_2 n_3} \tag{A.9}$$

In these equations

$$x_{ij} = \frac{1}{n_3} \sum_{k=1}^{n_3} x_{ijk} \tag{A.10}$$

and

$$x_i = \frac{1}{n_2} \sum_{j=1}^{n_2} x_{ij} \tag{A.11}$$

The variance for real sequential sampling is

$$\sigma_{\text{po}}^2 = \frac{K_1 - n_1}{K_1 - 1} \frac{s_1^2}{n_1} + \frac{1}{n_1} \frac{K_2 - n_2}{K_2 - 1} \frac{s_2^2}{n_2} + \frac{1}{n_1 n_2} \frac{K_3 - n_3}{K_3 - 1} \frac{s_3^2}{n_3} \tag{A.12}$$

The test equations are the same as in full sequence calculations.

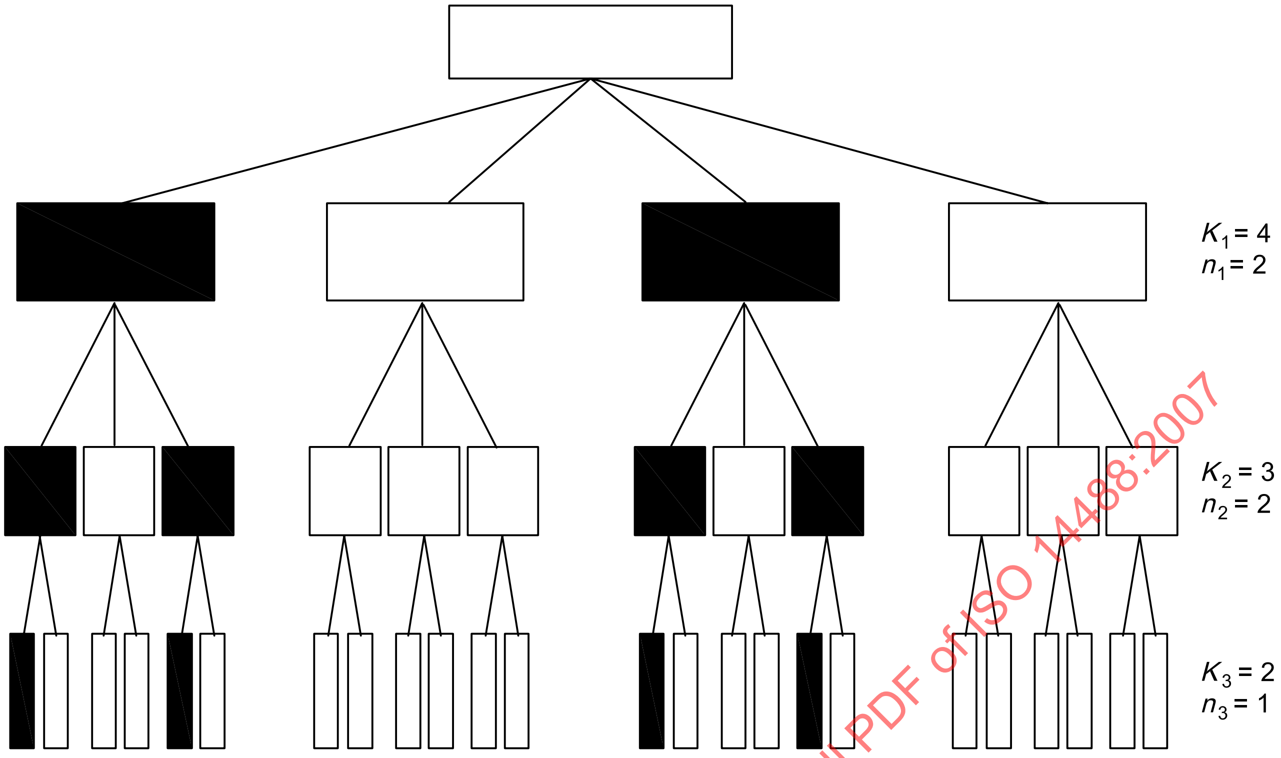


Figure A.2 — Partial sampling sequence — Example in three stages

Annex B
(informative)

Estimation of sampling errors and minimum mass of sample

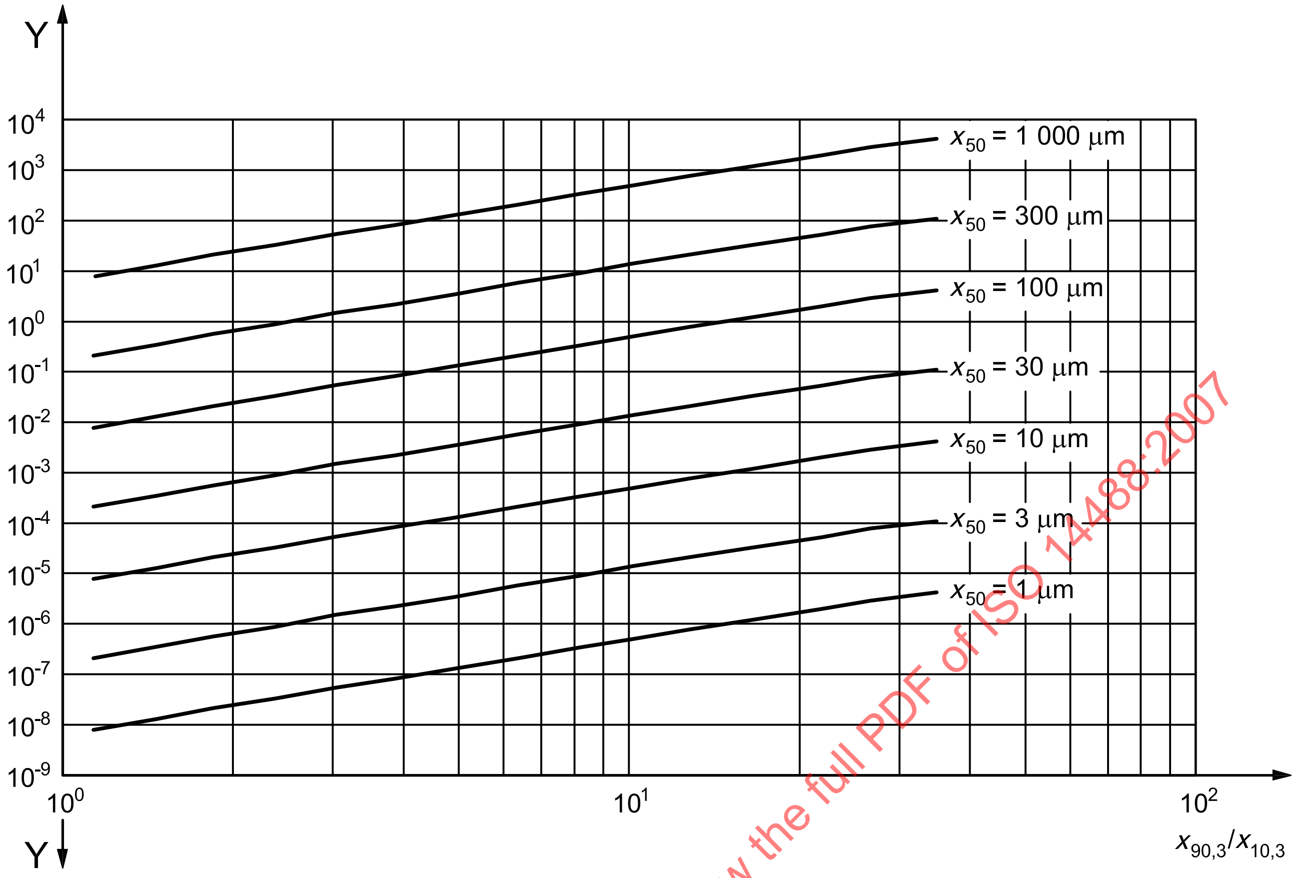
B.1 General

This annex provides examples of how to estimate sampling errors and the minimum mass of sample required for a stated precision. Generally, the total sampling error consists of two parts: a fundamental error (FE), which is due to the particulate nature of the material, and a segregation error, which is caused by segregation of the material. In Clause B.2 of this annex, a graph is presented which relates, in the case of a log-normal particle size distribution, the sample mass required for a 3 % fundamental error in the quantity of material larger than $x_{90,3}$ to the median particle size and the width of the distribution. Clause B.3 gives an example of the calculation of the sample mass needed for a 3 % fundamental error when sampling glass beads. Clause B.4 converts a fundamental error in the quantity of oversized material into that for the corresponding characteristic size. Clause B.5 presents an example of the calculation of the total sampling error from a series of measurements. Clause B.6 summarizes a procedure for estimating the minimum amount of sample (increment) and the minimum number of samples/increments needed to reach a given precision for a given value in a particle size distribution. Equations and background are given in the main text of this International Standard and in References [1], [2], [3], [4], [5], [7], [8], [9] and [10].

B.2 Graphical representation of sample mass required for a fundamental error of 3 %

In Figure B.1, the lines indicate, for a log-normal size distribution, the sample mass required to reach a fundamental error of 3 % in a quantity of material larger than $x_{90,3}$ in relation to the median size and the width of the distribution. The width of the distribution is expressed as the ratio between $x_{90,3}$ and $x_{10,3}$, and the material is assumed to have a true density of 1 000 kg/m^3. Figure B.1 gives a quick indication of the sample mass required to obtain an FE of 3 % in the amount above $x_{90,3}$, provided that an adequate estimate of the particle size distribution is available.

Figure B.1 also illustrates the considerable increase in the required sample mass as the particle size and/or the width of the size distribution increases. In the sub-micrometre region, the minimum sample mass is about 1 µg; for millimetre-sized particles it is about 0,1 kg to 1 kg. For materials having a true density higher than 1 000 kg/m^3, the sample mass has to be multiplied by the known particle density divided by 1 000.



Key

Y sample mass required (g)

Figure B.1 — Graphical representation of sample mass required for a fundamental error of 3 %

B.3 Example of the calculation of the sample mass needed to obtain a 3 % FE when sampling glass beads

This example illustrates a procedure for the calculation of the sample mass required to reach a stated precision for the FE in a quantity of material larger than a stated characteristic size in a size distribution. The example uses a precision (coefficient of variation) of 3 % for the fundamental error and $x_{90,3}$ as the characteristic size. Other values may be chosen.

It is assumed that the variance of the fundamental error and the number of particles n_0 are related in accordance with Poisson statistics [see Equation (2)]:

$$\mathrm{Var}(n_0) = \sigma(n_0)^2 = n_0$$

$$\sigma(n_0) = \sqrt{(n_0)}$$

and

$$\mathrm{CV}(n_0) = [100\sqrt{(n_0)}]/n_0\ \%$$

$$\mathrm{CV}(n_0) = 100/\sqrt{(n_0)}\ \%$$

Thus, for a precision of 3 %, the number of particles greater than $x_{90,3}$ will require $n_0 = 1\ 111$.