TECHNICAL SPECIFICATION

ISO/TS 14411-1

First edition
2017-05

Preparation of particulate reference materials —

Part 1: Polydisperse material based on picket fence of monodisperse spherical particles

Préparation des matériaux de référence à l'état particulaire — Partie 1: Matériaux polydispersés composés d'un ensemble de particules sphériques monodispersées

Reference number
ISO/TS 14411-1:2017(E)

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee TC 24, *Particle characterization including sieving*, Subcommittee SC 4, *Particle characterization*.

Introduction

The measurement of the particle size distribution can be accomplished by a number of techniques which measure some 1-D characteristic of the particle and usually equate this to an equivalent size assuming ideal shapes (usually spherical). Thus, these techniques usually require or assume knowledge of some other constant in order to calculate the particle size distribution. Each of these techniques measures different properties which makes the equivalent particle size a method-defined measurand. Comparability of results therefore requires application of the same methods, which in turn requires standardization.

This unsatisfactory situation of fundamental lack of comparability could be improved by a better understanding of the effects influencing the various methods. Since the sample material represents the link between the different methods, it is of central importance that it should meet as many physical assumptions of the considered methods as possible. A feasible approach is mixing known amounts of spherical, monodisperse particle fractions to create a polydisperse mixture ("picket fence distribution").

The individual particles should be spherical, as many sizing methods assume the particles to be spherical. Using particles that are in fact spherical fulfils this assumption, so the results of the various methods should be the same as far as the particle shape is concerned. A further advantage of spherical particles is that their size can be described by a single parameter only, the particle diameter.

The individual fractions of the mixture need to be monodisperse, as only then it is possible to trace the particle diameter back to the standard meter with an acceptable uncertainty and to get mixtures of theoretically known particle size distributions in the end.

These materials should be used as follows.

The monodisperse particle fractions can be used to demonstrate equivalence of results with these ideal particles. If a method gives deviating results, the method is not yet fully understood and further investigation of the deviation is needed. The polydisperse mixtures can be used to challenge measurement methods to see what the output is. Final outcome should be a comprehensive understanding of the methods including particle dispersion, particle transport, physical principle and evaluation leading to better comparability of results. The approach described in this document is based on Reference [22] and Reference [23].

A second approach is developing a theoretical framework for more accurate measurement of particle size distributions. Also, this approach is fundamentally limited to spherical particles of equal density, to be applicable to different methods.

This document describes preparation protocols of picket fence distributions of spherical, quasi-monodisperse particulate reference materials.

Preparation of particulate reference materials —

Part 1:
Polydisperse material based on picket fence of monodisperse spherical particles

1 Scope

This document describes the preparation of polydisperse spherical particles based on a picket fence of quasi-monodisperse reference materials, the characterization of its monodisperse components with acceptable uncertainty and the estimation of the uncertainty of the mixture of these particles. This type of material is normally suitable for all particle characterization methods within the appropriate limits of the techniques. An example of using these reference materials in a reliability calculation for a mass-based cumulative size distribution is provided.

This document limits itself to the technical specificities of preparation beyond the general requirements for certified and non-certified reference materials as described in ISO Guide 30, ISO Guide 31, ISO Guide 35 and ISO 17034.

2 Normative references

There are no normative references in this document.

3 Terms, definitions and symbols

3.1 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at http://www.iso.org/obp

3.1.1
aspect ratio
ratio of minimum Feret diameter to the maximum Feret diameter of a particle

[SOURCE: ISO 26824:2013, 4.5, modified]

3.1.2
pycnometry
method wherein particle density is obtained from the measured mass of sample with a given calibrated volume

[SOURCE: ISO 26824:2013, 2.4]

3.1.3
apparent particle density
particle mass in the dry status divided by the volume it would occupy including all pores, closed or open, and surface fissures

[SOURCE: ISO 13317-4:2014, 3.1]

3.1.4
hydrostatic balance
method to measure particle density based on particle dynamic sedimentation velocity with known fluid density and viscosity condition

3.1.5
reference material
material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process

[SOURCE: ISO Guide 30:2015]

3.1.6
certified reference material
reference material (3.1.5) characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability

[SOURCE: ISO Guide 30:2015]

3.1.7
nominal value
designated diameter in terms of a target value in a given specification

Note 1 to entry: The nominal value is the target diameter for an individual picket as calculated from the upper and lower size of the *picket fence distribution* (3.1.8), the number of pickets and the requirement of equal spacing of pickets on a lognormal scale. Actual values may differ from the nominal ones due to the availability of suitable material

3.1.8
picket fence distribution
mixture of several monodisperse particle fractions (pickets)

3.2 Symbols

Symbol	Quantity	Unit	Derived unit
α_i	Particle mass fraction for the suspension of picket *i*	kg/kg	mg/kg
$\alpha_i^{(0)}$	Particle number fraction for the suspension of picket *i*	—	—
Δx_i	Particle size interval in size range *i*	m	µm
δ	Uncertainty of the parameter given in the index NOTE: In other fields of measurement science and ISO/IEC Guide 98–3 (GUM), the symbol *u* is used instead.	—	—
δx_i	Uncertainty of the size x_i	m	µm
g	Parameter defined by Formula (A.1)	—	—
M	Parameter used in Formula (A.5)	—	—
m_b	Mass of the vessel for the dry mass determination	kg	mg
m_d	Dry mass (vessel and particles) in the dry mass determination	kg	mg
m_i	Mass of suspension *i* used for the preparation of the picket-fence distribution	kg	mg

Symbol	Quantity	Unit	Derived unit
$m_{l,i}$	Mass of solvent of picket *i*	kg	mg
$m_{p,i}$	Mass of particles of picket *i* in suspension	kg	mg
m_s	Mass of suspension used for the dry mass determination	kg	mg
$m_{x,i}$	Mass of the particles of picket *i* in the final picket fence distribution	kg	mg
N, N_i	Total number of particles and particle number of picket *i*	—	—
n_i	Number of particles in size range *i*	—	—
n_{picket}	Total number of pickets	—	—
p	Total number of uncertainty factors	—	—
$q_0(x)$	Density distribution by number	m^{-1}	μm^{-1}
$q_3(x)$	Density distribution by volume or mass	m^{-1}	μm^{-1}
$Q_0(x)$	Cumulative distribution by number	—	—
$Q_{0,i}^*$,$Q_{3,i}^*$	True cumulative distribution by number and mass with logarithmic abscissa	—	—
$Q_3(x)$	Cumulative distribution by volume or mass	—	—
ρ_i	Particle density of picket *i*	$kg\ m^{-3}$	$g\ cm^{-3}$
s	Standard deviation of the particle size distribution	m	µm
s_g	Geometric standard deviation	—	—
u	Parameter used in Formula (6) to give confidence level, u = 1,96 for 95 % probability reliability NOTE This corresponds to the coverage factor k in ISO/IEC Guide 98–3 (GUM).	—	—
x, x_i	Particle diameter and particle diameter in size range *i*	m	µm
x_l	Diameter of the smallest picket	m	µm
x_u	Diameter of the largest picket	m	µm
$x_{50,0,i}$ $x_{50,3,i}$	Median diameter of particle *i* based on number and mass	m	µm
$x_{50,3}$	Median particle size of cumulative volume or mass distribution	m	µm
$x^*_{50,3}$	Most reliable median particle size of a cumulative volume or mass distribution with logarithmic abscissa	m	µm

4 Material requirements for preparing the individual monodisperse fractions

4.1 General description

The material of the individual pickets shall be suitable for particle size measurement using image analysis methods within dry or aqueous environment.

4.2 Requirements on the general properties of the material for individual pickets

The material of the individual pickets shall meet the following requirements.

a) The particles shall be spherical without significant macroscopic concavities, outgrowths or pores.

The aspect ratio of all particles shall exceed a value of 0,95. A typical mean aspect ratio should be 0,97. Alternatively, the ellipse ratio shall exceed 0,95, a typical value should be 0,97 or above.

b) When dispersed in pure water, no colour bleeding is allowed. The optical homogeneity of the material is very important to be as uniform as possible. This applies for the particles within one monodisperse fraction, as well as for a comparison of the particles of two different monodisperse fractions.

c) The particle surface should be smooth without any contaminations or adhesions.

d) The apparent density of the material has to exceed the density of the dispersing liquid for the particles not to float in wet applications. Furthermore, the apparent density should not be too high for avoiding sedimentation effects. Therefore, a value within the range above 1 000 kg/m^3 and smaller than 2 500 kg/m^3 seems to be optimal for aqueous applications. Particles of higher densities can be used if a liquid with higher density or viscosity is used.

   The apparent density of the material is important to be as constant as possible for different particle sizes. Variations of ±0,5 % with respect to the mean value of the apparent density may be accepted.

e) The material should not contain any kind of fragmented particles or coarse outliers, e.g. agglomerates. Any other material coming in contact with the particles should not be dyed by adhering dust or abrasion.

f) The particles shall have a high chemical stability and be non-soluble in dispersant media.

g) The material should be easily dispersible in the chosen liquid. No particle agglomerates or flocculation should be detectable after dispersion. It is allowed to support the particle dispersion using dispersing agents or ultrasound.

h) The particles should not be disrupted by ultrasound pressure in dispersant media. The mechanical strength should be as high as possible since the material should be able to withstand a typical dry dispersion procedure without getting crushed. Nevertheless, it is not possible to define a concrete value since there are several different dry dispersion procedures not allowing for a reliable theoretical calculation of stress parameters.

i) The particles should not agglomerate under normal environmental conditions. Their electrostatic behaviour should allow for using them, e.g. on a vibratory chute without adhering to the chute itself.

j) The material should provide a shelf life of at least two years after production without appreciably changing its physical properties. All important storage conditions have to be known, e.g. necessary UV-protection/light-protection.

k) The swelling of the material suspended in pure dispersant media should be as low as possible. In any case, it should not exceed a value of 0,8 % referred to the particle diameter in dry condition. The swelling behaviour shall be specified in the sample preparation procedure

l) The size of the particle-liquid interface in dispersion should be negligible compared to the particle diameter.

5 Characterization of the individual monodisperse fractions

5.1 Particle size distribution

Particle size should be determined by a method that provides traceable results. The requirements for the individual methods are given below.

— Results shall be traceable to the International System of Units (SI) either by using CRMs with traceable reference values or by being calibrationless.

— The methods shall be validated in a way that allows estimation of a measurement uncertainty.

— Uncertainty estimates for the various size fractions are available.

— All results and characteristic values have to be given in terms of a volume-based particle size distribution, $Q_3(x)$.

It should be ensured that the measured particle size distributions do not overlap. This is achieved if each distribution meets the following requirements:

a) The distribution width given in terms of the ratio x_{90}/x_{10} should be 1,12 or smaller.

b) The actual mass median particle diameter of each mono-disperse fraction should not deviate by more than 4 % from the nominal diameter calculated from the lognormal distribution.

c) The uncertainty of the actual mass median particle diameter, calculated from traceable results from a suitable optical method, $x_{50,3}$, should be in the range of 0,99 $x_{50,3}$* to 1,01 $x_{50,3}$* with 95 % reliability where $x_{50,3}$* is the most reliable mass median diameter. Larger uncertainties will result in larger uncertainty for the final distribution.

It is possible to compensate for not meeting one of the above criteria by setting stricter limits on others. For example, a higher ratio x_{90}/x_{10} is permissible if the actual mean particle diameters deviate less than 4 % from the nominal ones. Regardless of failing to meet an individual requirement, the basic requirement of non-overlapping distributions shall be met.

5.2 Aspect ratio

The aspect ratio should be measured by a suitable optical method measuring at least 10 000 particles by random sampling. Fewer particles would not allow demonstrating fulfilment of the criteria set for the aspect ratio.

5.3 Density

The particle density should be measured by pycnometry or hydrostatic balance.

5.4 Refractive index

The refractive index shall be measured by any suitable method, e.g. by the liquid immersion method.

6 Preparation of picket-fence distributions

6.1 General

A picket-fence distribution should include at least one complete decade in particle size.

A picket-fence distribution should contain an uneven number of mono-disperse fractions and not less than 7 different mono-disperse particle fractions within a range of one decade of particle size. All fractions should be equally spaced on a logarithmic scale.

The nominal diameter x_i of picket i is calculated from the lower diameter, x_l, the upper diameter, x_u, and the total number of pickets, n_{picket}, using Formula (1):

$$x_i = x_l \cdot 10^{(i-1)\frac{\log(x_u)-\log(x_l)}{n_{picket}-1}} \quad (1)$$

All pickets should consist of the same material to minimize differences in density or optical properties.

6.2 Preparation of individual pickets

6.2.1 General

In most cases, it will be impossible to weigh the particles as dry powders due to the intrinsic uncertainty of weighing. In addition, many particles are distributed as suspensions, so drying and weighing increases the risk of agglomeration.

NOTE The uncertainty of the balance alone for weighing 1 mg with an analytical balance (display 0,000 00 g) is about 15 %. Using a microbalance, this uncertainty is typically reduced to less than 0,5 %, but static influences (e.g. incomplete transfer from the weighing boat to the final vessel) increase this uncertainty.

If direct weighing is possible, 6.2.2 and 6.2.3 can be skipped. For particles available as suspensions, 6.2.2 can be skipped.

6.2.2 Preparation of suspensions from dry powders

Weigh an appropriate amount of the dry powder ($m_{p,i}$) into a known amount ($m_{l,i}$) of the chosen solvent and homogenize according to the instruction of the particle producer. The particle mass fraction of picket *i* is calculated as Formula (2):

$$\alpha_i = \frac{m_{p,i}}{m_{p,i} + m_{l,i}} \tag{2}$$

6.2.3 Determination of the particle mass fraction of suspensions

For particles available as suspensions, the particle mass fraction shall be determined. Follow the following steps.

a) Clean and dry a vessel and determine its mass, m_b.

b) Weigh an appropriate amount of the suspension (m_s) into the vessel. The amount taken should not contain less than 500 mg of solids.

c) Slowly evaporate the solvent to achieve constant mass (m_d). The final drying temperature should be high enough to evaporate all solvent, but should not cause shrinkage of particles. If in doubt, contact the provider of the suspension for appropriate drying conditions. Constant mass is achieved when subsequent weighings differ by less than 1 mg.

d) Determine the particle mass fraction of picket *i* in the suspension as given in Formula (3):

$$\alpha_i = \frac{m_d - m_b}{m_s - m_b} \tag{3}$$

6.3 Preparation of a picket fence distribution

6.3.1 General

Picket-fence distributions shall be prepared as “one-shot” materials directly from gravimetric weighing of the individual pickets to avoid errors from subsampling of a homogenized sample. The uncertainties of the weighing should be less than 0,1 % of the weighed mass.

6.3.2 Preparation from dry powders

Weigh equal masses of the dry powders for each picket, $m_{x,i}$, into a vessel and homogenize.

NOTE This is the simplest approach for the preparation of a picket fence distribution, but the accuracy of weighing sets a limit to the use of this approach.