INTERNATIONAL STANDARD

ISO 14887

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Sample preparation — Dispersing procedures for powders in liquids

Préparation de l'échantillon — Procédures pour la dispersion des poudres dans les liquides

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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.

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 14887 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 and B of this International Standard are for information only.

Introduction

The evaluation of particle size distribution is of crucial importance for research projects, product development, process control, quality control, and other technical activities where particle size effects are important. Paints, inks, filled plastics, ore processing, pharmaceuticals, agricultural and cosmetic products depend on accurate particle size analysis for their commercial production.

A typical powder is composed of clumps of “primary" particles that are held together by weak or strong forces. The size of clumps remaining after the powder has been wetted into a liquid depends in part on how much energy has been expended in breaking up these clumps. Since a clump responds to most particle sizing methods as a large particle would, the presence of clumps in incompletely dispersed samples skews the reported particle size distribution to larger sizes than if all the clumps were broken up. A particle size analysis is useful only if the sample is prepared so that the particles are in a well-defined degree of dispersion, preferably one in which most clumps are fully deagglomerated and in which the particles do not reagglomerate or adhere to the walls of the sample container during the time required for analysis.

While "complete" dispersion to primary particles is often desired, it is important to remember that in many cases the most useful information is obtained when the sample is not fully dispersed. For example, if a customer blends the powder into a liquid using a low-shear process that does not break moderately strong bonds in the clumps, the quality control tests for powder intended for that customer should use similarly low shear during sample preparation and analysis.

Because of the impurities present, the equipment available for breaking up clumps, the methods used for particle size analysis, and the dispersing agents available for testing may vary from one site to another, the procedure developed at one site by applying the guidelines in this International Standard may differ from (but be as valid and as useful as) that developed at another site for the same powder.

A list of references for further study, including standards for evaluation of some of these more complex systems, is given in the bibliography.

Annex A discusses some of the complications that arise

— when the powder has a surface treatment or soluble components;

— when the liquid contains ionic or polymeric solutes;

— when the dispersing agent contains minor ingredients.

Annex B covers the classification of commercial dispersing agents in the various dispersing agent categories.

Sample preparation — Dispersing procedures for powders in liquids

1 Scope

This International Standard was developed to help particle size analysts make good dispersions from powder/liquid combinations with which they are not experienced. It provides procedures for

— wetting a powder into a liquid;

— deagglomerating the wetted clumps;

— determining if solution composition can be adjusted to prevent reagglomeration;

— selecting dispersing agents to prevent reagglomeration;

— evaluating the stability of the dispersion against reagglomeration.

This International Standard is applicable to particles ranging in size from approximately 0,05 to 100 µm. It provides a series of questions on the nature of the powder and liquid involved. The answers are used with charts that guide the user to generic dispersing agents that are likely to be suitable for dispersing the powder in the liquid.

This International Standard applies only to the preparation of simple, dilute dispersions (less than 1 % by volume solids) for particle size analysis. It does not deal with the formulation of complex and commercial mixtures highly loaded with solids, such as paints, inks, pharmaceuticals, herbicides and composite plastics.

2 Normative reference

The following normative document contains provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the normative document indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 8213:1986, *Chemical products for industrial use — Sampling techniques — Solid chemical products in the form of particles varying from powders to coarse lumps.*

3 Terms and definitions

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

3.1
agglomerate
assemblage of particles which are loosely coherent

SEE **floc** (3.5)

3.2
aggregate
assemblage of particles rigidly joined together

NOTE Because of the confusion which exists in the use of the above terms they are used sparingly throughout the text.

3.3
clump
assemblage of particles which are either rigidly joined or loosely coherent

3.4
critical micelle concentration
CMC
concentration of dispersing agent above which micelles will form

3.5
floc
assemblage of particles which are very loosely coherent

SEE **agglomerate** (3.1)

3.6
primary particles
units that are to be measured in the particle size analysis, in general harder to break than clumps

3.7
Tyndall effect
light scattered perpendicular to a beam of light passing through a liquid that contains particles

4 Symbols and abbreviated terms

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

S_V	Volume-specific surface area (m^2/kg)
CMC	Critical micelle concentration (mol/m^3)
IS	Ionic strength (mol/m^3)
$M_{-1,3}$	Complete –1-th moment of the density distribution of particle volume
PEO	Polyethoxy = $(-CH_2-CH_2-O-)_n$
PPO	Polyisopropoxy = $(-CH_2-CH(CH_3)-O-)_n$
pH_{iso}	pH at which the zeta potential is zero for an amphoteric surface (which is positively charged at lower pH and negatively charged at higher pH)
pK_a	pH at which half the hydrogen ions from acid groups are ionized
pK_b	pH at which half the hydroxide ions from base groups are ionized
$\overline{q}_{3,i}$	Density distribution of particle volume
x_i	Upper particle size of the i-th particle size interval (m)
µm	Micrometer
ζ	Zeta potential [V]
®	Registered trade name.

5 Examination of the dry powder

5.1 Sampling

Sampling shall comply with the requirements specified in ISO 8213, unless a method specified in a national standard or mutually agreed upon by the analyst and client takes precedence. Sample preparation shall always be done consistently so that repeated preparations based on replicate samples of a batch of powder (which was carefully mixed before being sampled or subdivided into samples) give closely comparable results.

5.2 Clump size range and particle size range

Sprinkle the dry powder on a microscope slide and examine it using an optical microscope at × 200 magnification or other suitable magnification. Put a cover glass over the powder on the microscope slide and tap the cover glass lightly with a spatula (take care to avoid breaking the cover glass) to see how easy it is to crush the clumps. Note the approximate size range of the clumps that are not broken up by such crushing. If the majority of the particles are smaller than 1 µm, use a transmission or scanning electron microscope to observe and characterize the particles.

5.3 Shape and surface roughness; their variation with size

Note whether the surfaces of the fundamental particles are spherical or crystalline, smooth or rough, porous or nonporous. Determine whether all the sizes of particle have the same morphology. If the particles are very rough or porous, obtain an experimental measure of the volume-specific surface area (m^2/kg). If this value is large compared to the area computed for spheres with the powder's particle size distribution then an unusually large amount of dispersing agent (compared to a similar size distribution of spherical nonporous particles) may be required to stabilize the dispersion.

NOTE The volume-specific surface area of spheres may be calculated from

$$S_V = 6M_{-1,3}$$ (equation 35 in ISO 9276-2)

where

$$M_{-1,3} = \sum_{i=1}^{n} \overline{q}_{3,i} \ln \frac{x_i}{x_{i-1}}$$ (equation 31 in ISO 9276-2)

6 Selection of a liquid and trial dispersion

6.1 Selection of a liquid

The analyst shall list the liquids that are commonly used for dispersing the solids for the selected method of particle size analysis and shall strike from the list any that fail to satisfy the following criteria.

— If the method is sedimentation, the liquid shall have a specific gravity that differs sufficiently from that of the powder to permit the use of this method.

— If the method is light scattering, the liquid shall have a refractive index (at the analytical wavelengths) that differs sufficiently from that of the powder to permit the use of this method.

— The liquid shall have negligible reactivity with the powder.

— The liquid shall not swell or shrink the particles by more than 5 % in diameter.

— The liquid shall provide a solubility of less than 5 g of powder per 1 kg of liquid.

NOTE This is to minimize Ostwald ripening that could cause the particle size distribution to change during the measurement time.

— The liquid shall have a change in the solubility (for the powder) with temperature of less than 0,1 mg/l per kelvin, or the temperature shall be controlled throughout the preparation and analysis to keep the solubility from changing by more than 0,5 mg/l.

NOTE If the particle size analysis method requires 10 mg of powder dispersed in 1 litre of liquid, a temperature rise of 5 K (from an ultrasonic probe or particle-analysis instrument warmth) would cause the dissolution of 1 mg or 10 % of the powder.

6.2 Preparation of a test paste of the powder

Put two drops (or 0,1 g) of the liquid on an etch-roughened glass plate ("frosted" glass). Blend in a roughly equal amount of powder by sprinkling powder on the liquid surface and rubbing it into the liquid using a circular motion of a 10 mm wide spatula, applying a moderate amount of pressure (sufficient to read 1 kg on the scale of a balance). The objective is to wet all the powder surfaces and to break up all clumps of powder into primary particles. The high concentration of solids provides crowded conditions that favour collision between clumps and breakup into primary particles. These crowded conditions will also favour flocculation unless the particles repel one another.

6.3 Preparation of a dilute dispersion of the powder

Make a dilute dispersion (4 % by mass) from the concentrated paste by adding a few drops at a time of the liquid and blending in with the spatula until 50 drops (about 2,5 g) of liquid have been added. This quantity should be sufficient for examination with a microscope. If a larger quantity is required for other types of test, the analyst shall follow the instructions given in 7.2.

7 Examination of the dispersion

7.1 Evaluate for under- or over-grinding

Examine the dilute dispersion using an optical microscope (for particles larger than 1 µm in diameter) or an electron microscope (for particles smaller than 1 µm in diameter). Use × 200 magnification with the optical microscope and view the particles by transmitted light.

Note whether the clumps originally seen in the dry powder have completely broken up during the procedure for making the paste and diluting it. If not, the analyst shall make a new dispersion using ultrasonic treatment (see 9.2). The analyst shall evaluate this new dispersion and increase, as needed, the energy put in to breakup clumps until full dispersion is attained.

Note what fraction of primary particles have become broken during the procedure for making the paste and diluting it. If the fraction of particles broken is over 5 %, the analyst shall make a new dispersion by simply stirring the powder into the liquid. The analyst shall evaluate this new dispersion and increase the energy put in to breakup clumps as needed until full dispersion is attained with less than 5 % breakage of primary particles (see 9.2).

Record the conditions that avoid under- or over-grinding and use these to prepare dispersions for evaluation until the clump breakup process is optimized according to the procedures in 7.2.

7.2 Evaluation of stability

7.2.1 Introduction

If the suspending liquid has a viscosity below 10 mPa·s and the particles are well-dispersed, very small particles will appear to move randomly in the microscope's field of view. Particles in the 1 µm to 5 µm range are best for observing this effect. Note that, even if the powder consists mostly of larger-size particles, there are likely to be a few particles inside the 1 µm to 5 µm range that can indicate whether or not the dispersion is stable. If the particles are smaller than 1 µm some other form of evaluation shall be used, such as measuring the rheological stress-strain

cycle of a 10 % by volume solids dispersion from 0,1 s^{-1} to 100 s^{-1} to see if it exhibits hysteresis (indicative of structure formation and breakage) or not (in which case the dispersion is stable).

Observe the dilute dispersion using the optical microscope. Note what happens when two particles come close together. Rate the stability as good if the particles repel each other rather than coming into contact. Rate the stability as marginal if the particles collide and stay together briefly before separating again. Rate the stability as poor if the particles collide and remain in contact to form a permanent floc. If the stability is good, no added dispersing agent is required to form a stable dispersion. If the stability is marginal or poor then either solution conditions (such as pH) shall be changed or a dispersing agent shall be added to provide stability.

Other methods for evaluating dispersions are noted in annex A. If microscopy and the other techniques are not feasible then particle size analysis may be used to evaluate stability. If a series of analyses separated by several hours lie within the reproducibility of the instrument (determined using a dispersion that is known to be stable) then the sample dispersion may be considered to be stable.

7.2.2 Notes on optical microscopy

Optical microscopy is the simplest and most effective way of evaluating the degree of deagglomeration and the stability of dispersions containing particles that are above 1 µm in size. Note that particles whose refractive index is close to that of the liquid will not provide enough contrast to be viewed with the optical microscope. At a solids concentration of a few percent, well-dispersed particles will appear to behave as separate entities. As the cover glass is moved sideways over the surface of the slide, note whether the particles in the dispersion move individually and not as a bonded group. Note whether particles that are below about 5 µm in size may exhibit "Brownian motion", as particles move about erratically due to unbalanced collisions of the particle with molecules of the surrounding fluid.

Particles smaller than the limit of optical resolution (about 0,3 µm) appear as bright spots when they are illuminated from the side with a dark field behind them ("ultramicroscopy"). Although the width of the spot is indeterminate, the size of the particle responsible for the spot may be estimated by its Brownian motion: the more actively a spot moves, the smaller the particle creating the spot. The size of the smallest detectable particle using this technique depends on the scattering power of the particles. Particles of titanium dioxide or of a metal as small as about 0,02 µm may be observed using this technique, but for oil droplets the limit of observation is about 0,1 µm.

Dispersion stability is destroyed if the particles stick to the glass microscope slide. This is a particular problem for positively charged particles, since glass is normally negatively charged. Such adhesion can also invalidate the measurement process, especially for light-scattering methods where the amount of solid circulating for analysis may be so small that it is completely removed by adsorption on the walls of the sample circulation system. In such cases, one can chemically treat the glass (with a cationic adsorbate such as dodecyl trimethyl ammonium bromide) so that it becomes positively charged and thus prevents deposition of the particles being analysed.

7.2.3 Notes on electron microscopy

Evaluation by electron microscopy requires that the dispersion be spread out on a thin support film and dried. As the liquid evaporates and the liquid surface shrinks between two particles, surface tension can pull previously well-dispersed particles into contact to form a clump. This problem can be minimized if the analyst can use a liquid with a low surface tension. Dispersion stability shall be judged as good if the particles are well spread out on the grid and bad if they are found mostly in clumps.

7.3 Evaluation of any flocs formed

If flocs have formed, put a cover glass over the dispersion on the microscope slide. Use a spatula to push the cover glass gently from the edge to slide it over the dispersion and apply shear force to the flocs. Note whether the flocs break up and how rapidly they reform. Flocs are reversible if they break up under shear and then reform similar flocs. Flocs are unstable if shear causes large, loose flocs to roll up into small, tight flocs. Flocs are strong if they do not break up with gentle sliding. In the last case, the addition of dispersing agent may not be effective unless a high shear force can be applied to break the floc in the presence of dispersing agent.

8 Identification of possible dispersing agents

8.1 Wetting of the solid particle by the liquid

The control of the wetting process allows the adhesion forces to be modified between the particles and the binding forces produced by liquids in the intermediate capillaries to be partially modified.

The general aim for particles size analysis is a spontaneous wetting as complete as possible. This can be searched by two ways:

— low-interfacial tension liquid/gaseous by wetting agents;

— low-interfacial tension solid/liquid by hydrophilizing agents.

In the case of insufficient wetting, a simultaneously mechanical treatment can be recommended (highly intensive ultrasonic treatment of the suspension, kneading of the system as a plastic mixture with a spatula).

8.2 General principles

Subclauses 8.2 to 8.4 explain the principles used in developing the decision charts in 8.5. Complete dispersion of a powder in a liquid occurs when the individual particles that made up the original clumps have become separated, move independently of each other, and remain separated from one another. This requires that there be no attractive force between the particles as they approach one another. If there is an attraction then the solid/dispersion will exhibit non-Newtonian flow and have a yield stress (i.e. the dispersion will be able to support a finite shear stress without any flow occurring.) Most of the indirect tests of dispersion rely on this effect. For example, a dispersion with a yield stress enables settling particles to form an open structure which does not collapse under the force of gravity. Such a dispersion will settle to form a higher sedimentation volume (lower sediment density) than a completely dispersed system would.

Highly anisotropic particles form a more or less rigid gel at very low concentrations of solids when there is a net attractive force between the particles.

8.3 Charge stabilization

8.3.1 Introduction

Particles which bear a surface charge will repel each other if the electrostatic repulsion is larger than the polarizability attraction (also called the Hamaker or Van der Waals attraction). A surface charge corresponding to a zeta potential greater than 30 mV is generally sufficient to provide a stable dispersion. Charge stabilization is the best way to stabilize dispersions in which the liquid has a relative dielectric permittivity greater than 30 (methanol at room temperature has a relative dielectric permittivity of 33, water of about 80) and an ionic strength less than 0,1 mol/l (i.e. a low concentration of ions in solution).

8.3.2 Surface ionization

The charge on the particle may arise from ionization of surface groups (influenced by the pH of the solution). For example, surface amine groups will adsorb a hydrogen ion from solution and become positively charged if the pH is below the pK_b for the powder. Surface carboxyl groups will lose a hydrogen ion and become negatively charged if the pH is above the pK_a for the powder. Amphoteric surface groups, such as the OH groups found on a metal oxide or hydroxide, will adsorb a hydrogen ion and become positive if the pH is below the pH_{iso} for that oxide and will lose a hydrogen ion and become negative if the pH is above the pH_{iso}. The dependence of hydrogen ion adsorption on pH is such that (when the ionic strength is below 0,1 mol/l) the zeta potential generally becomes large enough to stabilize a dispersion if the pH is two or more units away from pH_{iso}.

8.3.3 Differential dissolution of lattice ions

If the powder is ionic and does not dissolve significantly in the liquid, the presence of a soluble salt of one of the ions making up the powder may result in the adsorption of the common ion. For example, a sodium bromide solution will disperse silver bromide in water and a potassium hydrogen phosphate solution will disperse calcium hydroxyapatite in water. Since these soluble salts do not reduce the surface tension of water significantly, they are not classified as surfactants.

8.3.4 Adsorption of multiply charged ions

If the powder is ionic or has highly polar bonds and the liquid is water, multiply charged ions which are **not** part of the crystal lattice may be adsorbed to form a charged surface of soluble salts. Examples are the polyphosphate, hexametaphosphate, pyrophosphate and polysilicate ions. Since the salts involving these ions do not reduce the surface tension of liquids in which they are dissolved, they are not classified as surfactants.

If the powder is a nonpolar organic material and the liquid is a polar organic material, surface ions can be created by adding a neutral ion-pair to the system. The ion-pair adsorbs on the particle surface and then dissociates into ions, one of which desorbs to leave a charged particle. For example, the additive trimethyldodecylamine hydroxybenzoate dissociates to form an aliphatic quaternary amine (cationic) and a polar organic acid (anionic).

8.3.5 Adsorption of surfactant ions

Organic powders suspended in water can become charged by adsorbing the organic ion of a surfactant, leaving the inorganic counter-ion in solution. Organic amines adsorb a hydrogen ion to become positively charged if the pH is below the pK_b; organic acids lose a hydrogen ion to become negatively charged if the pH is above the pK_a. Zwitterionics and amino acids have a more complex dependence of charge on pH. The dependence of ionization on pH is such that (when the ionic strength is below 0,1 mol/l) the zeta potential generally becomes large enough to stabilize a dispersion if the pH is more than two units above the pK_a of a hydrogen-ion-releasing material or if the pH is more than two units below the pK_b of a hydrogen-ion-accepting material surface.

8.4 Steric stabilization

This is usually the best way to stabilize dispersions in which the liquid has a relative dielectric permittivity less than 30 or an ionic strength greater than 0,1 mol/l (i.e. a high concentration of ions in solution).

NOTE Methanol at room temperature has a relative dielectric permittivity of 33.

Magnetic particles have long-range attractive forces that cannot easily be shielded by additives. Dispersions of such particles may be stabilized using reactive anchors attached to polymeric chains of high molecular weight that are soluble in the dispersing fluid.

Steric dispersing agents may be anionic, cationic or nonionic dispersing agents or block copolymers. Their molecules usually consist of an anchor section and a backbone section. The anchor is designed to absorb on the solid: for example alkane chains or aryl groups will adsorb on organics. The backbone is designed to be soluble in the liquid: for example poly(ethylene oxide) chains are soluble in water. Soluble polymers that do not adsorb or that adsorb weakly shall be avoided, since these can cause depletion flocculation and can make dispersion even harder to achieve.

8.5 Procedure for selection

The procedure for identifying possible dispersing agents for testing is as follows.

a) Use 8.4.1 to determine the powder category for the powder being analysed.

b) Use 8.4.2 to determine the liquid category for the liquid being used to suspend the powder.

c) Use 8.4.3 to determine the dispersing agent category for the chosen combination of powder and liquid categories

NOTE Some categories of solid and some categories of dispersing agent are charged only in specific pH ranges when the suspending liquid is water. The effectiveness of that charge in stabilizing the system depends on the ionic strength of the solution. These factors are incorporated in the columns labelled Condition and Dispersing-agent category in Table 1.

d) In the dispersing agent listing category, find one or more specific materials that are in the dispersing agent category that was recommended as likely to be effective.

8.5.1 Determination of the powder's category

Solid	Category
activated carbon	hydrogen-bonding organic
NOTE Activated carbon has a high specific surface area and the surface is often oxidized.	
adipic acid	organic acid (pK_a = 4,5)
alumina → see aluminium oxide	
aluminium	metal
NOTE In air, the surface of aluminium becomes aluminium oxide.	
aluminium hydroxide → see boehmite	
NOTE There are several other types of aluminum hydroxide.	
aluminium oxide	metal oxide (pH_{iso} = 9,2)
anatase → see titanium dioxyde	
barium sulfate	ionic salt
boehmite	metal hydroxide (pH_{iso} = 8,3)
boron carbide	weakly polar
boron oxide	metal oxide
cadmium sulfide	ionic salt
calcium carbonate	ionic salt
calcium phosphate	ionic salt
calcium sulfate	ionic salt
carbon (see also activated carbon)	metal
carborundum → see aluminium oxide	
cellulose	H-bonding organic
cement	metal oxide
chalk → see calcium carbonate	
charcoal → see activated carbon	
clay → see silicate minerals	
copper	metal
corundum → see aluminium oxide	
feldspar	metal oxide
flour	H-bonding organic
fluorinated hydrocarbon	fluorocarbon
fly ash	metal oxide (pH_{iso} varies with type)
glass	metal oxide (pH_{iso} varies with type)
graphite → see carbon	
gypsum → see calcium sulfate	
iron	metal (surface may oxidize in wet air)
iron oxide	metal oxide (pH_{iso} = 6,8)
iron sulfide	ionic salt
NOTE Because HS- is a weak acid, sulfides behave like oxides in aqueous systems and have an isoelectric point.	
kaolin → see clay	
latex (polystyrene)	nonpolar organic
lead	metal
lead oxide	metal oxide
limestone → see calcium carbonate	
magnesium	metal (surface may oxidize in wet air)
magnesium oxide	metal oxide
mica → see clay	
naphtylamine	organic amine (pK_b = 9,8)
nickel	metal

nickel oxide	metal oxide
paraffin	nonpolar organic
perfluoroalkane	fluorocarbon
pollen	H-bonding organic
polyester	polar organic
polymethylmethacrylate	polar organic
polyvinyl chloride	polar organic
protein	H-bonding organic (pH_{iso} = 6,5)
pyrite → see iron sulfide	
quartz → see silica	
resin	H-bonding organic
rutile → see titanium dioxide	
sand → see silica	
shale → see clay	
silica	metal oxide (pH_{iso} = 2,4)
NOTE Silica gel has a very high surface area and may have been treated with organics to make the surface hydrophobic. In that case, treat it as a nonpolar organic.	
silicate minerals	metal oxide
silicon carbide	weakly polar
silver	metal
silver halide	ionic salt
silver oxide	metal oxide (pH_{iso} = 5,7)
soil	
NOTE Soil is a mixture of components and varies widely. Classifying it as sand may not work for all variations.	
starch	H-bonding organic
steel → see iron	
sugar	H-bonding organic
talc → see silicate minerals	
NOTE Commercial forms may have hydrophobic surface treatments.	
Teflon® → see perfluoroalkane	
titanium dioxide	metal oxide
tungsten carbide	weakly polar
zinc	metal
NOTE In air, the surface may oxidize to zinc oxide.	
zinc oxide	metal oxide
zinc sulfate	ionic salt
zirconium oxide	metal oxide

8.5.2 Determination of the liquid's category

Liquid	**Category**
acetone	highly polar
alcohol → see specific type (methanol, ethanol, etc.)	
butanol → see *n*-butanol or sec-butanol or *t*-butanol	
chlorinated hydrocarbon (except perchloro)	weakly polar
cyclohexane	nonpolar
cyclohexanone	polar
decahydronaphthalene (decalin)	nonpolar
dodecane	nonpolar
ethanol	highly polar
ethanol/water (< 5 % mass water)	highly polar
ethanol/water (5 % to 50 % mass water)	H-bonding organic
ethanol/water (> 50 % mass water)	water
ethyl acetate	weakly polar
ethylene glycol	H-bonding organic
fluorinated hydrocarbon	nonpolar
hydrocarbon solvent	nonpolar

iso-octane	nonpolar
isopropanol → see propan-2-ol	
methanol	highly polar
methanol/water (< 5 % mass water)	highly polar
methanol/water (5 % to 50 % mass water)	H-bonding organic
methanol/water (> 50 % mass water)	water
methyl ethyl ketone	weakly polar
methyl isobutyl ketone (MIBK)	weakly polar
2-methyl-propan-2-ol	H-bonding organic
n-butanol	weakly polar
n-octanol	H-bonding organic
propan-2-ol	highly polar
propan-2-ol/water (< 5 % mass water)	highly polar
propan-2-ol/water (5 % to 50 % mass water)	H-bonding organic
propan-2-ol/water (> 50 % mass water)	water
t-butanol → see 2-methyl-propan-2-ol	
toluene	nonpolar
water	water

8.5.3 Determination of the category of a prospective dispersing agent

Table 1

Solid category	Liquid category	Condition	Dispersing-agent category
metal	water		PEO/mercaptan
		Encapsulation in gelatine is also effective	
	organic		organic amine
carbon	water		PEO/alcohol
	organic		PPO/alkane
metal oxide	water	IS < 0,1	adjust pH < pH_{iso} – 2 or pH > pH_{iso} + 2
		IS > 0,1	polyion
	organic		organic acid or organic amine
metal hydroxide	Use the same guidelines as for a metal oxide		
ionic salt	water	IS < 0,1	try common-ion effect
		IS > 0,1	polyion
	H-bond organic		PEO/PPO copolymer
	highly polar		PEO/PPO copolymer
	weakly polar		PEO/alkane
	nonpolar		PEO/alkane
protein	water	IS < 0,1	adjust pH < pH_{iso} – 2 or pH > pH_{iso} + 2
		IS > 0,1	polyion
	organic		phospholipid
organic acid	water	IS < 0,1	adjust pH > pK_a + 2
		IS > 0,1	phospholipid
	organic		polyester/polyacrylate
organic amine	water	IS < 0,1	adjust pH < pK_b – 2
		IS > 0,1	phospholipid
	organic		polyester/polyacrylate
H-bonding organic	water		PEO/PPO copolymer
	organic		phospholipid
highly polar	H-bonding organic		PEO/PPO copolymer
	highly polar		PEO/PPO copolymer
	weakly polar		PEO/alkane copolymer
	nonpolar		PEO/alkane copolymer

Table 1 *(continued)*

Solid category	Liquid category	Condition	Dispersing-agent category
weakly polar	water		polyionic or polyester
	H-bonding organic		PPO/alkane copolymer
	highly polar		PPO/alkane copolymer
	weakly polar		PPO/alkane copolymer
	nonpolar		PPO/alkane copolymer
nonpolar	water	IS < 0,1; pH < 5	quaternary amine salt
		IS < 0,1; pH 5 to 8	organic sulfonate
		IS < 0,1; pH > 8	organic acid salt
		IS > 0,1	phospholipid or PEO/siloxane
	H-bonding organic		PPO/alkane copolymer
	highly polar		PPO/alkane copolymer
	weakly polar		PPO/alkane copolymer
	nonpolar		not needed
fluorocarbon	water		perfluoro-organic acid
	organic		PPO/alkane copolymer

8.5.4 Identification of commercial sources of dispersing agents

See annex B for a partial listing of commercial suppliers of formulations whose major active component is one of the prospective dispersing agents determined in 8.5.3.

9 Optimization of the dispersion method

9.1 Introduction

Day-to-day variations in materials and procedures may cause variations in the degree of dispersion. Consequently, it is important to carry out particle size analyses on a number of replicate samples and to observe the dispersions under a microscope to see if the procedure is reproducible (successive replicates agree closely) and robust (modest variations in measurement procedure result in only minor changes in the result).

9.2 Comparison of the effectiveness of possible dispersing agents

Put about 50 mg of the dispersing agent (one drop) on a ground glass plate. Add about 100 mg of the liquid (two drops) and mix them well with a spatula.

Continue even if some of the dispersing agent does not dissolve.

Add about 100 mg of the powder (about the same volume as the liquid) and mix it into the liquid with the spatula. If the powder is resistant to breakage (as determined from the previous examination with a microscope), put pressure on the spatula so as to break up clumps. Gradually mix in about 2,5 g more of the liquid (50 drops), then wash the paste off the plate and into a beaker using a mix of 0,1 g of dispersing agent in 100 g of the liquid. Evaluate the stability of the particle size distribution using a particle size analyser. Stability shall be considered good if the particle size analysis is comparable to microscope analysis and repeat runs taken an hour apart agree within the repeatability of the size analysis method. See annex A for other tests of the degree of dispersion.

9.3 Optimization of the method of breaking up clumps

9.3.1 Notes on ultrasonic treatment

Ultrasonic cavitation can break up clumps of powders with less grinding action than occurs during spatula-aided wetting. Ultrasonic cavitation can be applied to laboratory dispersions from a probe or a bath. Alternating pulses of vacuum (that can pull the liquid apart to form evacuated cavities or microvoids in the liquid) and pressure (that causes the cavities to collapse) are created at frequencies from 10 kHz to 10 MHz, depending on the equipment. These cavities are nucleated by surfaces, so they are created where they can best help break the bonds holding clumps together. The collapsing cavities generate high-temperature plasmas near the bubble wall, and these plasmas can cause chemical changes on the particle surface or in the solution.

Ultrasonic baths create a pattern of active zones where cavitation takes place, and each of these has a low concentration of cavities. In an ultrasonic bath, much of the cavitation energy is expended in regions of the bath outside the sample vial. Ultrasonic probes create a single active zone with a high concentration of cavities. For a given energy input, an ultrasonic probe will break up the clumps in a given volume of sample faster than an ultrasonic bath will. Ultrasonic probes are more likely to cause particle fracture than ultrasonic baths. In both cases, it is necessary to ensure that the powder sample is circulated through the active zone, since that is the only place that clump breakup can occur.

9.3.2 Management of heat buildup during clump breakup

Ultrasonic probes and other devices to break clumps can add considerable heat to the sample, raising its temperature and thus increasing the solubility of the solid and consequently making the observed size smaller. The heat input, during the time needed to pass all the dispersion through the probe's active zone enough times to achieve full dispersion, may be sufficient to boil the liquid away. If the temperature rise exceeds 5 K during breakup of the clumps, the process shall be carried out in a vessel that is actively cooled to eliminate or minimize the temperature rise.

9.3.3 Determination of the optimum range for clump breakup energy

The mechanical energy (the product of power and time) put into the system to achieve breakup of the clumps may also cause breakage of the primary particles that make up the clumps. High-velocity liquid jets are formed during the collapse of ultrasonic-cavitation-induced microvoids in a liquid if the voids are near a particle surface. These jets can damage fragile crystals. This is a particular problem for elongated crystal shapes, such as needles and plates. The analyst shall run a series of clump breakup tests at various energies to establish the optimum energy region for dispersion, which is above the energy levels that are inadequate to fully break up all the clumps and below the energy levels that damage primary particles.

9.3.4 Documentation of the optimum breakup conditions

The analyst shall select conditions falling within the optimum energy region for dispersion and specify the following parameters:

a) a descriptive name for the powder to indicate composition and source;

b) the name of the method of particle size analysis for which the dispersion is being prepared;

c) a descriptive name for the liquid to indicate composition and source;

d) type and dimensions of ultrasonic bath or probe;

e) level and material used as fill in the ultrasonic bath;

f) volume and type of container to be used to contain the dispersion;

g) quantity of liquid;

h) quantity of dispersing agent;

i) quantity of powder;

j) initial temperature of the sample mixture;

k) position of the ultrasonic probe with respect to the container centreline and liquid level or position of the container with respect to the ultrasonic bath corners and position of the sample liquid level with respect to the bath's liquid level;

l) size, type, and location and revolutions per minute of stirrer in the sample;

m) rate and temperature of coolant circulation in any cooling jacket;

n) power setting and mode (continuous or intermittent, time switched on and off during cycles);

o) duration (total time) of the ultrasonic treatment;

p) final temperature of the sample mixture.

The analyst shall use these specified conditions to ensure reproducibility when preparing dispersions of the powder for particle size analysis.

9.4 Determination of the optimum quantities to use

NOTE Several factors limit the acceptable upper limit of the quantity of dispersing agent in the liquid.

— Micelles, droplets or particles of undissolved dispersing agent may be counted as particles of the sample powder by the particle size analyser.

— The powder may have a high solubility in micelles or droplets of the dispersing agent, and any such dissolution will change the particle size distribution of the powder.

Since adsorbed dispersing agent does not contribute to the chemical potential for forming micelles, a larger quantity of dispersing agent is required to leave enough in solution to achieve 80 % of the critical micelle concentration (CMC). This may mean that the initial mixture of dispersing agent and liquid will contain micelles, droplets or particles of the dispersing agent, but these will dissolve when the powder is added and the dispersing agent is adsorbed on the powder surface.

If the solubility, CMC and adsorption per unit area on the powder surface (at 80 % of the CMC or solubility) of the dispersing agent are known, the quantity of dispersing agent shall be calculated as 80 % of the lesser of 1) its solubility or 2) its critical micelle concentration (CMC) in the liquid plus the amount adsorbed on the surface of the powder at the concentration of powder to be used in the particle size analysis.

If there is insufficient information for such a calculation, the following procedure shall be carried out to determine the optimum quantity empirically:

a) Prepare a series of mixtures with 0,1 g, 0,2 g, 0,5 g, 1 g, 2 g, and 5 g of dispersing agent in 1 litre of the liquid.

b) Reject any mixtures that are cloudy or show a Tyndall effect, evidence for the presence of undissolved material.

c) Filter the remaining mixtures to remove particles (dust, contaminants, etc.) that are larger than 0,2 µm.

d) Measure out 50 ml of each of the filtered solutions and 0,1 g of powder for each solution.

e) Mix each powder into its solution and break up clumps. As a starting point for optimizing the energy input, break up clumps using a 750 W ultrasonic probe in the intermittent mode (1 s on, 1 s off) for 60 s while stirring so as to make the particles circulate past the probe tip.

f) Analyse the particle size distribution of each dispersion (kept under constant stirring) three times a day (for example 8 h, 12 h, and 16 h) over a period of three days. Tabulate the volume-average size and standard deviation.

g) Note, as the minimum acceptable concentration of dispersing agent, the lowest concentration at which the volume-average size and standard deviation do not vary outside the limits of repeatability for the size-analysis method used.

h) If several dispersing agents are under study, reject any for which the particle size analysis is unstable at any dose or for which only a few dispersing agent concentrations give stable analyses.

The quantity of dispersing agent shall be specified as grams of dispersing agent per kilogram of liquid prior to the addition of the dispersing agent.

10 Maintenance of dispersion stability during sample handling

10.1 Stability during dilution

Size analysis often requires the use of very low concentrations of solids. If the particles have a solubility that would cause more than 1 % of the mass required for the analysis to dissolve, both the solution and the diluent should be saturated with the solid under study before adding the particles and doing the size analysis. If the dispersion is to be analysed at a temperature above room temperature, the solution may become unsaturated (due to increasing solubility with temperature) and some of the particles will dissolve, making the particle diameters smaller. The smaller particles will dissolve completely and the larger ones somewhat less. Even in a saturated solution, dissolution and precipitation occur continuously and simultaneously, with thermodynamics favouring the growth of large crystals and disappearance of small ones. Because of these conflicting phenomena, the final average size may be smaller or larger than the original.

The stability of a dispersion often depends on maintaining an adsorbed layer of stabilizing ions or polymer molecules on the particle surface. Dilution of such a system with the pure solvent may result in desorption of so much dispersing agent that what remains on the surface of the particles is not sufficient to make the dispersion stable. Such a desorption is less likely for polymeric dispersing agents of high molecular weight, since these are essentially irreversibly adsorbed. The possibility of loss of dispersion stability upon dilution is greatest for particle sizing methods based on light scattering, most of which require drastic dilution before a measurement can be made.

To avoid problems with desorption and dissolution of the solid, the analyst shall filter [or gently centrifuge] one portion of the dispersion and use the clear filtrate (or supernatant) for diluting other portions of the dispersion for analysis.

10.2 Stability during change in pH

Changing the pH of the sample, by dilution or otherwise, can have a profound effect on the stability of the sample. For systems which are stabilized by a surface charge (as is often the case for mineral oxides) the pH is a principal variable controlling the surface charge. The pH also controls the ionization of weak-acid dispersing agents, such as polyacrylic acid. Both the charge and the conformation (extended vs. tightly coiled) of many natural dispersing agents (particularly the proteins) will also be markedly affected by pH. Avoid or minimize changes in pH during sample handling, unless that change is known to be beneficial to maintaining stability.

Annex A
(informative)

Alternative dispersion-stability tests

NOTE Several recent publications discuss in detail a variety of methods for evaluating dispersions [8], [16], [22].

A.1 Sedimentation behaviour

If the dispersion is stable to reagglomeration because particles repel one another, the particles will move about during sedimentation so as to avoid contact, and the resulting sediment will be a densely packed array with minimum occluded liquid. Pour about 80 g of the dilute, well-mixed dispersion into a 100 ml graduated cylinder and observe the sharpness, rate of fall, and final height of the interface between relatively clear supernate (liquid above the sedimentation boundary) and the sediment bed. Centrifugation may be required to make small particles settle fast enough to complete the experiment in a reasonable time.

Well-dispersed particles will settle independently at velocities proportional to the squares of their diameters, so there will be no sharp dividing line between the sedimenting section and the supernate, which will normally be opalescent or turbid. Well-dispersed particles move independently past one another to form a densely packed bed with a small depth.

If the particles show residual attraction and are not completely dispersed, they will stick when they collide to form a network as they settle. Flocs settle more rapidly than single particles, and the resulting sediment bed will have a high porosity, so sediment depth is greater for flocculated systems than for well-dispersed systems. Highly anisotropic particles (disks or rods) may form flocs with volumes so large that they fill the vessel and the flocs do not settle at all.

A.2 Surface-charge density

For systems which are being stabilized by adsorption of an ionic surfactant or of inorganic ions such as phosphate, the parameter which measures the effectiveness of the procedure is the zeta potential of the particles. The zeta potential (written as ζ) measures the effective electrostatic potential difference between the particle surface and the bulk solution around the particle. It is a particularly important quantity for aqueous dispersions because it monitors the effective charge which one particle experiences when it moves near to another particle and so measures the repulsive force between them.

Zeta potential can be measured by determining the velocity of the particles in an electric field. The traditional direct microscopic technique has been superseded by more rapid and convenient methods based on light scattering or electroacoustics. These methods are, in principle, able to monitor both the size and zeta potential simultaneously, so a combination of minimum size and maximum (absolute value of) zeta potential can be taken as the best indication of complete dispersion.

If the stabilization of a dispersion is primarily due to electrostatic repulsion, measurement of the zeta potential can be a guide as to whether there is adequate electrostatic repulsion to overcome polarizability attraction. A common guideline is that the dispersion will be stable if zeta potential is greater than 30 mV. In electrophoresis, the applied electric field is held constant and particle velocity is monitored using a microscope and video camera. In the electrokinetic sonic amplitude technique, the electric field is pulsed, and the sudden motion of the charged particles relative to their counter-ion atmospheres generates an acoustic pulse which can be related to the charge on the particles and their size.

A.3 Rheology

Since a clump of particles contains occluded liquid, the effective volume fraction of a dispersion of clumps is larger than the volume fraction of the individual particles and there is less "free" liquid available to facilitate the flow than if the clumps were broken up. The viscosity of a dispersion containing clumps will decrease as the clumps are broken up. This method is not very sensitive in the final stages of clump breakup, when there are only a few small clumps left.

The effect of state of dispersion on the rheology (or flow behavior) of a dispersion is most evident for systems with concentrations of solids above 10 % by volume. It is instructive to plot shear stress as a function of shear rate, since the slope of the curve at any point is the viscosity of the dispersion at that shear rate. The plot is linear for a well-dispersed system of spheres, indicating that the viscosity does not change with shear rate.

The plot for non-spherical particles has decreasing slope with increasing shear rate. In other words, the viscosity of such systems decreases with increase in shear rate. These systems are said to be shear thinning. The usual explanation is that the particles become better aligned in the flow as the shear rate increases, so the flow becomes "easier" and so the viscosity is reduced. The effect is much more pronounced if the particles have attractive forces between them. Indeed, even spherical particles will show this shear thinning behaviour if they are not completely dispersed, and therefore the plot of shear stress as a function of shear rate can be used as an indication of the extent of dispersion.

Nonlinearity is usually accompanied by a finite yield value at zero shear. This value is called the yield strength. A non-zero value means that the dispersion is able to support a shear stress without undergoing any flow (impossible for a true liquid). The implications for flow can readily be observed by using a slow-speed magnetic bar to stir a dispersion with a finite yield strength: the upper surface of the fluid, located some distance from the influence of the stirrer, will remain stationary if the shearing stress produced by the stirrer at the surface of the fluid is not great enough to overcome the yield stress of the dispersion. Observations of this sort indicate that the system is not completely dispersed.

A.4 Attenuation of sound or electrical pulses

The attenuation of ultrasound (acoustic spectroscopy) or high-frequency electrical current (dielectric spectroscopy) as it passes through a dispersion will be different for well-dispersed individual particles than for flocs of those particles, because the flocs adsorb energy by breakup and reformation as the pressure or electrical waves jostle the flocs about. The degree of attenuation varies with frequency in a manner related to floc breakup and reformation-rate constants, which depend on the strength of the interparticle attraction, the size and density (inertia) of the particles and the viscosity of the liquid.

Annex B
(informative)

Commercial dispersing agents in the various dispersing agent categories

Table B.1 — Organic acids (and their alkali salts)

Dispersing agent	Commercial examples (manufacturer)
organic acid	Hystrene® (AC Humko)
PEO/fatty acid	5430 (Cognis), Lipopeg® (Lipo), Sipoic® (Speciality Industrial Prod.)
organic acid salts	Pationic® (Patco Additives)
organic acid salt with triethanolamine	Stepanol® WAT (Stepan)
sodium dodecanoate	Norfox® (Norman Fox)
sodium linoleate	Rhodaterge® (Rhodia)
sodium oxalate	Synchrowax® (Croda)

Table B.2 — Organic amines (and amides)

Dispersing agent	Commercial examples (manufacturer)
alkylamine	Kermamine® T (AC Humko), Armeen® (Akzo), (Pennwalt), Monamine® (Uniqema)
ethanolamine, triethanolamine	Numerous
PEO/long-chain alkylamine	Ethomeen® (Akzo) Witcamide® (Witco) Sipamine® (Speciality Industrial Prod.)
2-amino-2-methyl-propanol	Numerous
alkanolamide	Atlas® EM-16 (Uniqema), Monamid® (Uniqema) Witcamide® (Witco), Ninol® (Stepan), Standamid® (Cognis)
PEO/alkanolamide	Ethomid® (Akzo), Ethox (Ethox), Chemeen® (Chemax)
amino acid	Lexamine® (Inolex), Peptien® (Leiner Davis)

Table B.3 — Organic esters

Dispersing agent	Commercial examples (manufacturer)
fatty acid ester	Atlas® EM-17 (Uniqema), Lipogeg® (Lipo)
PEO/ester	Emulphor® EL (Rhodia), Lipopeg® (Lipo), Sipoest® (Speciality Industrial Prod.)
glycol esters	Dur-Pro® (Durkee), Witconol® RDC-D (Witco), Monalube® (Uniqema), Lipo (Lipo)
glycerol esters	Dur-Em® (Durkee), Santone® (Durkee) Myverol® (Eastman), Witconol® RHT (Witco), fish oils, Aldo® (Lonza Group), SipoEst (Speciality Industrial Prod.), Emerest (Cognis), Kessoc (Stepan)
lanolin	Atlas® G-1441 (Uniqema), Lipolan (Lipo), (Amerchol), (Fanning)

Table B.4 — Organic phosphate

Dispersing agent	Commercial examples (manufacturer)
alcohol phosphate	Albrite® TBPO4 (Albright & Wilson), Monofax® (Uniqema)
PEO/alcohol phosphate	Monofax® (Uniqema)

Table B.5 — Organic sulfate

Dispersing agent	Commercial examples (manufacturer)
sodium alkyl sulfate	Teepol®, Polystep (Stepan), Calfoam (Pilot), Rhodapon (Rhodia), Witcolate® (Witco)
alcohol sulfate	Duponol® (Witco), Standapol® (Cognis), Witcolate® (Witco)
alkyl phenol sulfate	Witcolate® (Witco), Atlas® (Uniqema), Triton® (Union Carbide)
sulfated triglycerides	Sulfonated GTO (Proctor)

Table B.6 — Organic sulfonate

Dispersing agent	Commercial examples (manufacturer)
sodium alkyl sulfonate	Siponate® SA (Rhodia), Witconate® (Witco), Emulgator® 30 (BASF)
sodium alkylbenzene sulfonate	Alkasurf® (Rhône-Poulenc), Ultrawet® (BP Amoco), AAS® (Vista), Polystep (Stepan)
sodium alkylnaphthalene sulfonate	Dispersol® T (Uniqema), Tamol® SN (Rohm and Haas), Alkanol® (Rohm & Haas), Sellogen® (Cognis)
sodium dioctyl sulfosuccinate	Aerosol® OT (Cytec), Emcol® 4000 (Witco), Monawet® MO series (Uniqema)
isethionate	Igepon® AC-78 (Rhodia)