



Introduction

A powder can be measured directly as a powder or dispersed in liquid when measuring particle size distribution by the laser diffraction technique. Measurement in the natural dry powder state is preferred when possible for reasons including generating results of the powder as used, minimal disposal and clean up (no liquid waste), and to avoid what might be a difficult liquid dispersion. Or a powder can be dispersed in a liquid if this provides a better approach for analyzing individual vs. agglomerated particles. Sometimes comparing the wet vs. dry results can confirm optimal dispersing conditions. If a certain air pressure setting using a dry powder feeder generates equivalent results to a well dispersed suspension measurement then the user has confidence both results are valid analytical procedures.

As always, the analyst should know the goal of the measurement. Is the interest to characterize a powder as it exists in the dry state, or is the goal to measure the individual particle state? Generating results indicative of the size distribution of the individual particles may require sample preparation steps if the powder particles are clumped together. This document focuses on lab techniques suggested to move from the state of clumps to individual particles.

Creating a well dispersed powder in liquid suspension can require up to four basic processes:

- Selection the liquid the powder will be dispersed in.
- Wetting the powder surface as it is placed in the liquid.
- Adding energy to de-agglomerate the particles.
- Stabilizing the mixture using appropriate chemistry.

A. Selecting the liquid

The first criteria for the liquid used for the particle size analysis is that the particles do not dissolve, swell, or otherwise change chemically in the liquid. Water is considered acceptable if the powder solubility is < 5 g powder in 1 kg of water. Other requirements include that the liquid should be free of bubbles and should have a viscosity low enough for easy recirculation through the instrument. High viscosity liquids are not only more difficult to recirculate, but also tend to be more difficult to clean from glass or quartz cell windows.

Of course water is the preferred liquid used for particle size measurements whenever possible, but solubility concerns or other considerations may require the selection of another solvent. Alcohol (IPA, ethanol, methanol) is a common next alternative and provides good results for many samples including cement, where hydration with water could cause serious problems if left in the instrument too long.

Less polar solvents are used when required, but may create challenges with disposal and exposure to the

analyst. Before choosing an organic solvent like hexane or other simple alkane as the next liquid to try, perhaps a food-based oil could provide an agreeable option. Some pharmaceutical compounds too soluble in water are analyzed in safflower oil – which may be higher in viscosity, but is more pleasant to be in contact with. Filtered mineral spirits may provide a less expensive option than reagent grade hexane.

The particle size analyzer can be used as a tool to test particle-solvent interactions when going through the dispersing liquid selection process. Basic repeatability measurements prior to complete method development can investigate if the sample is stable in a candidate solvent. Disperse the sample in the solvent, make multiple measurements, and review the data for indications of stability or lack thereof. If the particle size decreases steadily with time this could indicate dissolution. An increase in size over time could indicate the chosen chemistry causes aggregation or swelling. The HORIBA LA-950 Particle Size Analyzer software provides two calculations to quantify measurement stability, both of which could be used during the solvent selection process:

The coefficient of variation (COV) is defined as the (standard deviation/mean)*100. The COV of the median size, or D50, should be < 2% over three repeat measurements or the sample could be changing during analysis in the solvent.

The Chi square calculation checks the stability of the raw data on each channel, as well as the difference between the measured and theoretical light scattering intensity for each detector (1). A high Chi square value indicates fluctuation in the raw data during the measurement, therefore an unstable particle-solvent mixture.

B. Wetting the powder surface

An easy powder sample can be directly placed into water and measured without additional effort if the powder is naturally extremely hydrophilic. The degree to which a powder is hydrophilic or hydrophobic can be described

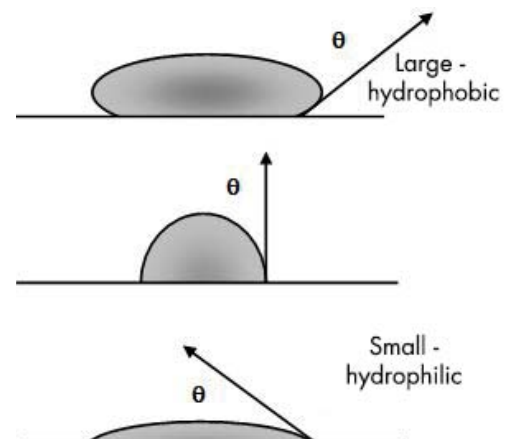


Figure 1: Contact angles for a drop of a liquid on a solid

using the surface chemistry term of contact angle. The contact angle is a measure of how well the liquid drop adheres to the surface of a solid (see Figure 1). Large contact angles indicate poor wetting ability - hydrophobic. Small angles indicate good wetting ability - hydrophilic.

Prior to analysis a small amount of powder can be added to a beaker containing water and observed by eye to qualitatively determine if the powder is naturally wetting. If it is not wetting easily it will float on the surface of the water as seen in Figure 2. If this is the case, then typically a surfactant is used to reduce the surface tension to improve wetting. Choosing a suitable surfactant is often done by trial and error in many labs, but if something is known about the sample then a more structured approach can be used. This requires basic understanding of both the powder and the categories of surfactants.



Figure 2: Left; non-wetted powder, Right; wetted after surfactant is added

Surfactants

A surfactant is a chemical acting as a surface active agent typically consisting of a polar head and a non-polar carbon-hydrogen chain. The non-polar hydrocarbon chain is typically hydrophobic while the polar head is typically hydrophilic. Surfactants are often classified by the type of polar head group as seen in Figure 3; non-ionic (no charge in the head group), anionic (negative charge), cationic (positive charge), and amphoteric or zwitterionic (two oppositely charged head groups).

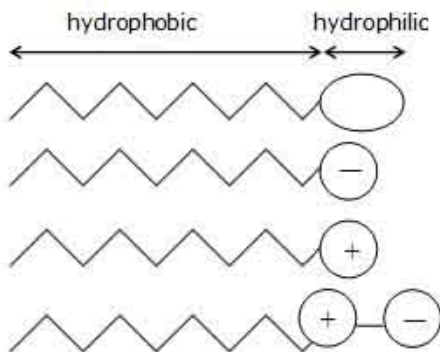


Figure 3: From top to bottom; nonionic, anionic, cationic and zwitterionic surfactants

Nonionic surfactants have no charge in the head group, but still exhibit surfactant properties. Common examples are long chain alcohols. Two of the most commonly used nonionic surfactants for powder sample wetting are Igepal CA-630 and Triton X-100.

Igepal CA-630 has replaced the use of Nonidet from the past and is chemically indistinguishable. The proper IUPAC name for Igepal CA-630 is octylphenoxy polyethoxy ethanol and the structure is shown in Figure 4. The hydrophobic portion comes from octylphenol and the hydrophilic head comes from different amounts of ethylene oxide.

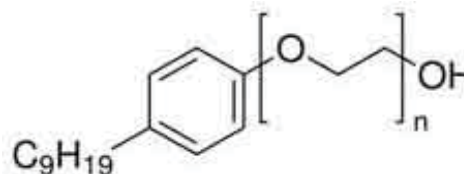


Figure 4: Chemical structure of Igepal CA-630

Triton X-100 is another commonly used nonionic surfactant, also known as polyoxyethylene octyl phenyl ether, with the structure shown in Figure 5. The hydrophilic chain has an average of 9.5 ethylene oxide units and a hydrophobic aromatic group.

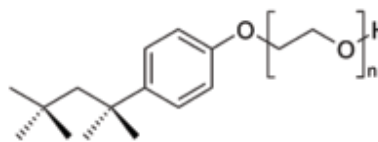


Figure 5: Chemical structure of Triton X-100

Other nonionic surfactants used as wetting agents in many particle characterization labs include Tween 20, Tween 80, Span 20, and Span 80. These surfactants have the added benefit for being edible, and are, therefore, used in many food and pharmaceutical products. Tween 20/80 also go by the names polysorbate 20/80.

Anionic surfactants

Anionic surfactants contain negatively charged functional groups at their head, such as sulfate, sulfonate, phosphate, and carboxylates. The anionic surfactant used the most in HORIBA application laboratories is Aerosol OT, or dioctyl sodium sulfosuccinate, whose chemical structure is shown in Figure 6.

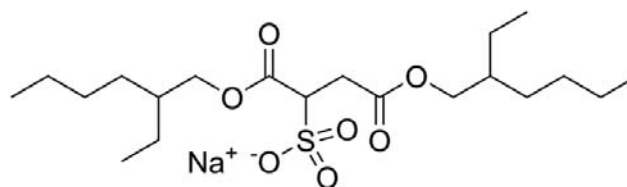


Figure 6: Chemical structure of Aerosol OT

Cationic surfactants

Cationic surfactants contain positively charged functional groups at their head that are typically primary, secondary, or tertiary amines. The hydrophobic carbon-hydrogen chain is typically C8 to C12. This surfactant category is often pH dependent. Primary amines become positively charged at pH <10 and secondary amines become charged at pH <4.

Zwitterionics (amphoterics)

Zwitterionic surfactants have both anionic and cationic centers attached to the same molecule. The cationic part is based on primary, secondary, or tertiary amines or quaternary ammonium cations. The anionic part can be more variable and often includes sulfonates. An example of a zwitterionic surfactant used in many food and pharmaceutical powders is lecithin, chemical structure shown in Figure 7. Lecithin is an edible surfactant, commonly made from soybean oil.

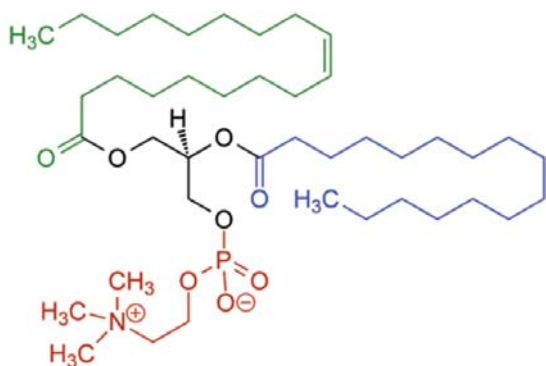


Figure 7: Lecithin

Surfactant selection

Sometimes just knowing the surface properties of the powder in liquid can direct the selection of which kind of surfactant to use for wetting to aid dispersion. Nonionic surfactants are often the first choice if nothing is known about the powder to be wetted. They tend to be more biocompatible, have lower sensitivity to electrolytes, and are helpful for both hydrophilic and hydrophobic surfaces.

Anionic surfactants may be a good option for surfaces that are positively charged. Since many biological surfaces are negatively charged, cationic surfactants adsorb strongly on them. While cationics can be very effective in dispersing natural products, they tend to be more expensive than anionic or nonionic surfactants. The pH dependence also adds a level of complexity for optimal dispersion.

Zwitterionic surfactants are useful for dispersing polar organics, biological products, fibers, and metals. These dispersions are best at pH > 6, where the amino acids are completely in the zwitterionic form.

A more complete description of surfactant selection to aid dispersion is given in ISO 14887 Sample preparation

– Dispersing procedures for powders in liquids (2) using the following approach:

1. Determine the category of the powder to be dispersed.
2. Determine the category of the liquid to be used.
3. Use Table 1 to determine the category of the dispersing agent.

Powders are broken into the categories shown in Table 1.

Powders	
Category	Example
metal	aluminum
metal oxide	aluminum oxide
ionic salt	calcium carbonate
H-bonding organic	cellulose
organic acid	adipic acid
non-polar organic	latex
weakly polar	silicon carbide
organic amine	naphthylamine
fluorocarbon	perfluoroalkane

Table 1: Powder categories (from ref. 2)

Liquids are broken into the categories shown in table 2.

Liquids	
Category	Example
water	water
non-polar	iso-octane
weakly polar	methyl ethyl ketone
polar	cyclohexanone
highly polar	acetone
H-bonding organic	ethylene glycol

Table 2: Liquid categories (from ref. 2)

Dispersants are broken into the categories in table 3.

Dispersants (incomplete)	
Category	Example
PEO/PPO copolymer	Pluronic
organic acids	sodium dodecanoate
organic amines	alkanolamide
organic esters	lanolin
organic phosphate	alcohol phosphate
organic sulfate	sodium alkyl sulfate
organic sulfonate	sodium alkyl sulfonate
phospholipid	lecithin
polyester	polyacrylate
polyionic salt	sodium silicate

PEO: Polyethoxy = (-CH₂-CH₂-O)-_n

PPO: Polyisopropoxy = (-CH₂-CH(CH₃)-O)-_n

Table 3: Dispersant categories (from ref. 2)

A cross reference table is then provided that matches the powder, liquid, and dispersant type. Table 4 shows a few examples from this table (thereby avoiding infringement on the ISO copyright.)

Powder	Liquid	Dispersing agent
H-bonding organic	water	PEO/PPO copolymer
H-bonding organic	organic	phospholipid
ionic salt	highly polar	PEO/PPO copolymer
ionic salt	weakly polar	PEO/alkane
metal oxide	water	adjust pH away from IEP
metal oxide	organic	organic acid
		or organic amine

Table 4: Cross reference table (from ref 2.)

Surfactant usage

The material given in ISO 14887 is valid for both electrostatic and steric stabilization of powders. This is a more rigorous approach than is typically used for just wetting powders in order to make particle size measurements. Most analysts making particle size measurements will just keep 3-6 surfactants in the lab and use them to wet powders prior to measurement. When approaching the measurement from this perspective first dilute the surfactant(s) to be used to about 10% in filtered DI water and mix until all of the surfactant has gone into solution. Dilution is always required in order to minimize bubbles once the sample is added to the instrument. Add a few drops of diluted surfactant onto a small amount of powder in a beaker. Then transfer the sample to the instrument or dilute further and use either an external ultrasonic bath or probe to aid dispersion prior to analysis.

C. Adding energy

Once the powder has wetted and is well dispersed the next step is to determine if energy is needed to break up agglomerates in order to measure the individual particles. This typically requires performing a particle size analysis and an investigation of results as a function of energy added to the system. The data interpretation for such a study is often both visual – looking at the result graph – and based on calculated results such as D10, D50, and D90 (3). The results shown in Figure 8 show overlays from measurements made without ultrasound (purple) and with different amounts of energy added (other colors). The amount of energy added in this example is number of seconds the ultrasonic probe was turned on in the LA-950, ranging from 0 to 180 seconds.

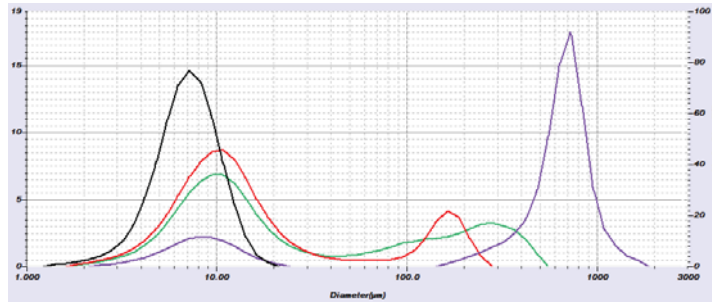


Figure 8: Effect of ultrasound on dispersing agglomerates

The careful use of ultrasound is an integral part of method development and is beyond the scope of this document focused on powder dispersion. Other HORIBA documents are available that address this subject in greater detail (4,5,6).

D. Stabilizing the mixture

Particles well dispersed by ultrasound as shown in Figure 8 may immediately begin to re-agglomerate depending on the surface chemistry of the dispersion. The surface chemistry can be altered to avoid re-agglomeration by adding a stabilizer chemical to the continuous phase. Adding a stabilizer such as sodium hexametaphosphate (structure shown in Figure 9) increases the charge on the surface of the particles (the zeta potential). Particles with a zeta potential high enough to offset the van der Waals attraction forces repel each other and are unlikely to re-agglomerate.

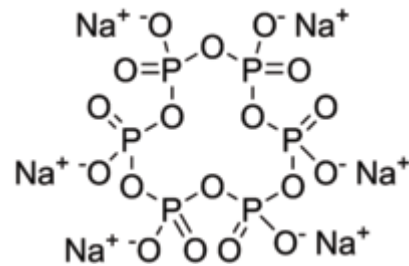


Figure 9: Chemical structure of sodium hexametaphosphate

The selection and concentration of the chosen stabilizer can also require a series of experiments in order to make an informed decision. Candidate stabilizer chemicals are shown in Table 5.

sodium	hexametaphosphate
sodium	pyrophosphate
sodium	silicate
sodium	citrate
sodium	tripolyphosphate
sodium	polyacrylate

Table 5: Stabilizers

The concentration of stabilizer can also influence the stability of the dispersion. Some standard procedures for soil analysis begin by dissolving 50 g of sodium hexametaphosphate in 1 L of water to be used as a 5% solution for dispersing the sample. This concentration may be much too high for many particle size analysis procedures, where concentrations from 0.01 - 1 % are more typical. A study of optimal stabilizer concentration can be performed either by making particle size measurements at different concentrations, or by direct visual observation of sample/stabilizer mixtures in beakers and noting which creates the most stable turbid mixture over time.

Case Study: Dispersing TiO₂ powder in water

Titanium dioxide powder (anatase) was sent to the HORIBA applications lab in France for analysis. The sample was prepared using the procedure shown below:

- 1 mL of Photo-Flo was added to 1L DI water to use as a wetting agent.
- 0.1 g (estimated) of TiO₂ powder is placed in a 250 mL beaker.
- 100 mL of Photo-Flo wetting agent is poured into the beaker.
- The sample is exposed to 60 sec of ultrasonic energy using an external probe

LA-950 settings:

- Refractive index: 2.500-1.00
- Concentration: T% (red laser) between 84-86%
- Pump & stirrer speed: 5
- Measurement duration: 5 sec

The sample was first analyzed using de-ionized (DI) water as the dispersing liquid. The measurement was repeated after waiting 30, 60, and 120 seconds after the initial measurement. The results are shown in Figure 10. Notice how the size increases with time – suggesting re-agglomeration of the particles.

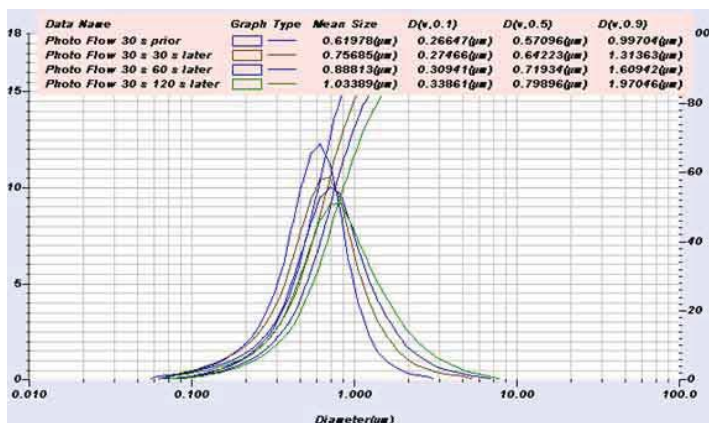


Figure 10: TiO₂ results vs. time in DI water

The same sample was next analyzed using 0.1 M sodium hexametaphosphate solution as the dispersing liquid. The measurement was repeated after waiting 30, 60, and

120 seconds after the initial measurement. The results are shown in Figure 11. Notice how the size does not increase with time – suggesting no re-agglomeration of the particles, or enhanced stability.

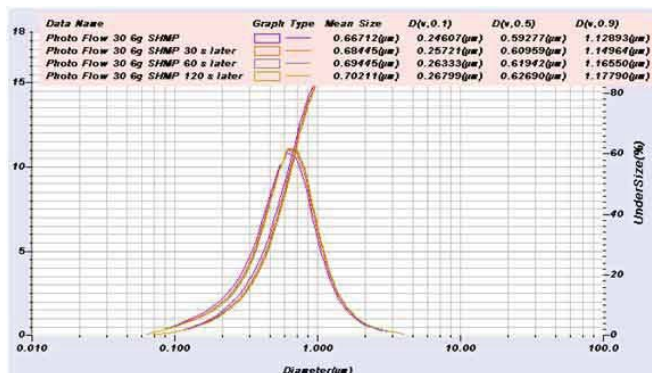


Figure 11: TiO₂ results vs. time in 0.1 M sodium hexametaphosphate

During the measurements a portion of the sample was removed for zeta potential analysis using the HORIBA SZ-100 DLS system. The sample dispersed in DI water had a zeta potential of -11.1 mV while the sample in sodium hexametaphosphate had a zeta potential of -47.5 mV as seen in Figure 12. The increase in zeta potential indicates higher dispersion stability – as observed during the particle size measurements performed on the LA-950.

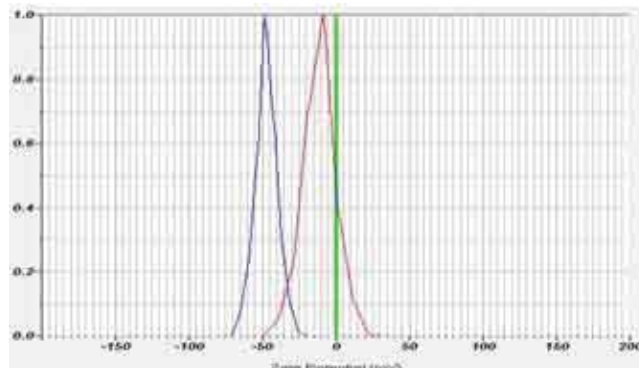


Figure 12: Zeta potential results for TiO₂ in DI water (red) and sodium hexametaphosphate (blue)

Conclusions

While trial and error may eventually lead to satisfactory powder dispersion for particle size analysis, understanding the sample and what is desired from the analysis can lead to a more scientific approach to method development. A well organized particle characterization lab will stock a number of the chemicals listed in this document, but a minimum of 3-4 surfactants and sodium hexametaphosphate should always be available for the kind of experiments described in this document. The amount of time spent on dispersion testing should be a risk based decision balancing method development time against the importance of accurate results.

Definitions

Dispersion: a two phase mixture of a continuous phase (the solvent) and the dispersed phase (the particles or emulsion droplets.)

To disperse: to create a two phase suspension or emulsion.

Clump: More than one particle stuck together as either agglomerates or aggregates.

Agglomerate: clump of particles that are loosely coherent.

Aggregate: clump of particles that are rigidly joined together.

Surfactant: A chemical acting as a surface active agent typically consisting of polar head and a non-polar carbon-hydrogen chain.

Primary particle: an individual particle as opposed to a clump, but preferably not broken by the sample prep or measurement process.

References

1. TN153 Understanding the Chi Square and Residual R Parameter Calculations, at <http://www.horiba.com/scientific/products/particle-characterization/download-center/>
2. ISO 14887 Sample preparation — Dispersing procedures for powders in liquids, at <http://webstore.ansi.org/>
3. TN156 Understanding and Interpreting Particle Size Distribution Calculations, at the Download Center.
4. AN151 Wet Method Development, at the Download Center.
5. Method Expert: Guided, Automated Method Development for the LA-950, at the Download Center.
6. Optimizing Ultrasound for Particle Size Analysis with the Method Expert.