



Introduction

Although any particle size analyzer will produce a result for every sample measured the desired goal is to generate meaningful, reproducible data. This requires that the sample analyzed be representative of the bulk material. In addition, errors must be minimized to assure reproducibility. Sampling - both primary and secondary - can be a critical component to the overall measurement strategy for reasons of both error/reproducibility reduction and result validity.

Sources of error during a particle size measurement include:

- Sampling; extracting a representative portion for analysis
- Sample preparation; dispersion
- Instrument settings and operator skill; many choices influence results
- Instrument induced; no instrument is perfect

The list of error sources above are listed in rough order of magnitude, depending on the material. There is a tradeoff between sampling and sample preparation, as shown in Figure 1.

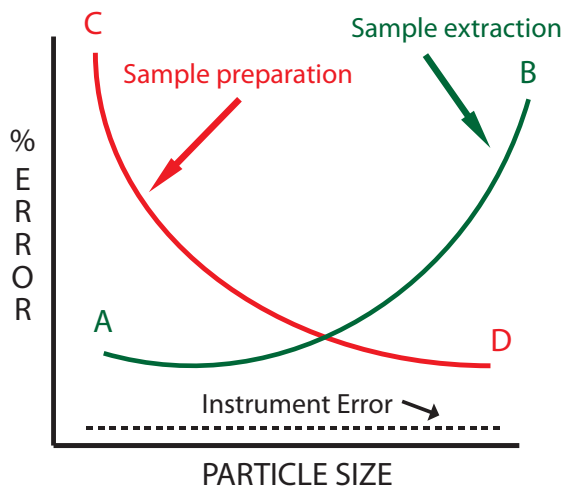


Figure 1: Error sources

The cross over point where sampling (sample extraction) becomes the critical component in additional error to the measurement process is sample dependent, but is typically assumed to be between 50 and 100 μm . Sampling also becomes more important as the breadth of the distribution increases.

A proper approach to sampling for particle size analysis requires a strategy. Companies may first consider a risk based analysis of the data generated. A researcher making rough measurements a few times a month has different needs than a plant that runs a unit operation such as milling based on the particle size distribution. If the laboratory in question operates within ISO 9001 guidelines, then the sampling procedures should be specified and documented. Another criterion to consider is which result is important and/or reported. If only the D50 is reported, sampling can be less important than if the D90, D95, etc. is a critical result.

The ultimate goal to keep in mind is to generate meaningful, reproducible particle size distribution (PSD) results. The results are only meaningful if the sample analyzed is representative of the whole - directly including the sampling methods. Reproducibility is the standard goal of robust particle size measurements, and sampling may be the largest source of error in the measurement depending on the material tested. The ISO 13320 (1) standard for laser diffraction defines acceptable reproducibility by requiring the sample be prepared and measured three independent times and for the coefficient of variation (COV) at the D10, D50, and D90 to meet these defined expectations:

- COV at the D50 < 3%
- COV at the D10 and D90 < 5%

Below 10 μm , these values are doubled, indicating how sample preparation and dispersion can cause additional errors at smaller particles sizes as seen in Figure 1.

Errors in sampling may lead to failing to meet either the goals set in ISO 13320, or internal specifications for a given material.

Powder segregation

One of the primary reasons sampling of powders for particle size analysis is important is the effect of segregation on the sample. As a powder mixture experiences vibration there is a change in the spatial uniformity of particle size distribution with larger particles migrating to the top and smaller particles migrating to the bottom. There are several

mechanisms at work, but the easiest way to visualize this phenomenon is simply that the smaller particles move downward under gravity as motion creates void spaces in the powder mixture. Size segregation is also observed when a powder sample is poured into a heap, or into a sample container. These effects are typically more pronounced in free-flowing rather than cohesive materials. The end result is that the sample arriving in the lab may require mixing at the least, to specialized sampling techniques for more difficult materials before analysis.

Primary and secondary sampling

Sampling prior to particle size analysis can be broken down into two steps:

Primary sampling is where a portion is removed from the bulk material. This could require removing the sample from a moving process stream, or from a container such as a drum or bag. This is an important step, but will not be discussed in this document which focuses on laboratory procedures. Readers wanting to investigate primary sampling can review the references (2,3,4) given at the end of this document.

Secondary sampling occurs in the laboratory and is therefore more under the control of the analyst. It is unusual for the entire sample that arrives in the lab be used for particle size analysis measurement. The lab operator must transfer a representative portion of the total into the instrument for analysis. This is the focus of this document. When secondary sampling powder, the goal is again to extract a representative portion to be used for the analysis. Ideally, this entire portion is placed into the instrument for measurement. The amount of sample used depends on whether the sample will be analyzed using a dry powder feeder, or dispersed in liquid.

Dry powder feeder approach

Much more sample can be analyzed (up to 50 grams for a high density powder) when using a dry powder feeder, than when dispersing the powder in a liquid (closer to 0.05 g for a low density powder). A dry powder feeder can measure small quantities when required, such as analysis of active pharmaceutical ingredients, or can analyze several grams of material when this will improve results. It is better to use more

sample for materials with a wider distribution. This provides for a better chance to measure the few large particles present in the material. Users should be aware that the vibrating tray feeding the sample into the instrument causes segregation. Therefore the best practice is to measure the entire portion placed on tray. This requires setting up the timing of the measurement and perhaps concentration range in order to optimize results.



Figure 2: Dry Powder Feeder

Powder dispersed in liquid approach

The powder can also be analyzed by dispersing the sample into a liquid to create a suspension. This approach creates a different set of challenges and may include the use of surfactants, finding the appropriate solvent, and the optimization of several instrument settings. If the powder disperses easily the operator may just dump sample directly into sampler. But if the sample is pre-dispersed first into a beaker, then we have added another step to the sampling; from the beaker into the instrument. The best practice is to transfer the entire sample in the beaker into the instrument. But if this is not possible, then a pipette is typically used for transport from beaker to instrument. See section on wet sampling on possible error sources and suggested best practices.

Sampling from a bottle

An untrained operator may simply remove powder from the top of the sample container and place the sample directly into the instrument, as seen in Figure 3. This is not best practice! Perhaps this will be acceptable for narrow distributions and easy samples, but in general this simplistic approach is the easiest way to maximize the sampling error.



Figure 3: Powder sampling from top of the bottle

Although this is not a suggested approach, if this is part of the sampling strategy then much of the potential error can be reduced by following these steps:

1. Mix the powder in the sample container by both rolling and tumbling as shown in Figure 4. Note that this is not effective if sample container is more than two thirds full.
2. After mixing to avoid errors due to segregation, use the spatula to remove a sample from close to the middle of the container.

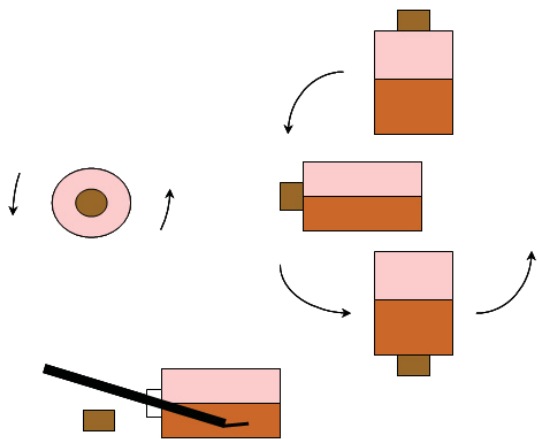


Figure 4: Bottle mixing and sample extraction

Sample splitting

The preferred approach for secondary sampling of powders is to use a sample splitting device to create equal portions, and then analyze one of the portions. Several kinds of devices are available for sample splitting, with several shown in Figure 5.



Figure 5: Static riffle divider (left) and spinning riffler (right) (5)

There are many models of both static riffle dividers and spinning rifflers to choose from. The size and/or internal dimensions of the device are typically associated with the size of the sample particles. The ISO 14488 document on sampling of particulate materials (2) provides guidance for selecting the opening width for static riffle dividers as shown in Table 1.

Particle max. size (mm)	Opening width (mm)
20-16	50
16-10	30
10-5	20
5-2.5	10
below 2.50	6

Table 1: Opening width for static riffle dividers (2)

It is advised to analyze the entire sample once divided, so several divisions may be required to obtain the proper quantity for the instrument. Two strategies are shown in Figure 6 if more than one split is required.

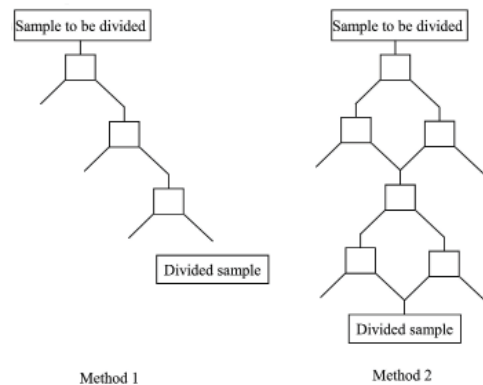


Figure 6: sample splitting strategies

In method one the primary sample is split into two, one of the parts is split again and so on. In method two the sample is divided into two parts and both parts are separately divided into two. Halves of the latter divisions are combined and divided in the same two-step manner until the proper amount is obtained.

Spinning rifflers provide the best approach to sample splitting of powders for particle size analysis. A vibrating tray transfers powder onto/into sample holders affixed to a turntable or divider ring.

The spinning riffler consists of a feed hopper, a vibratory feeder and a turn-table or other rotating divider ring where the sample holders are placed or attached to. The spinning riffler used in the HORIBA applications lab is designed for small sample quantities, as required for measurements in one of our laser diffraction analyzers. Larger spinning rifflers are suitable for splitting larger sample quantities. Care should be taken to assure that many rotations of the turntable are required to split the entire sample (the ISO document suggest 40 rotations, a large number in the opinion of this author), and keep the vibration rate constant during the riffling.

Cone and quartering is a manual approach to sample splitting and is sometimes the only option available for powders with very poor flow properties. The sample is poured onto a hard surface and then a quartering knife is inserted into the heap. A random quarter of the sample is then removed for analysis. This technique is not recommended for powders that segregate easily or are hazardous since the process can create dusting.

The choice between a static sample divider, spinning riffler or the cone and quarter method should be based on an understanding of the samples to be handled and the desired precision for the particle size analysis method. The classic study by Allen (3) on a mixture of sand and sugar particles is frequently cited and the results are shown in Table 2.

Technique	St. Dev
Coning & quartering	6.81
Stationary Riffing	1.01
Rotary Riffing	0.125
Random Variation	0.076

Table 2: Sampling technique and error standard deviation (3)

In the opinion of this author the sand/sugar mixture may present a close to worse case sampling scenario and error results. Although the purpose of this document is to inform and motivate readers to use best practice sampling techniques, the recent tests performed in the HORIBA application lab showed less variability than the classic study by Allen.

Case study 1

A powder sent to the Irvine, California applications lab for analysis was dispersed in water and analyzed three independent times (add to beaker, wet, pipette into instrument, measure, clean, repeat) on the LA-950 laser diffraction particle size analyzer. This sample set was measured by randomly removing a portion from the original container using a spatula. The results are shown in Table 2 and did not meet the reproducibility expectations at the D50.

LA-950 WET without Riffler

Sample Name	D(v, 0.1)	D(v, 0.5)	D(v, 0.9)
Run #1	3.080	38.018	203.416
Run #2	3.091	36.672	195.089
Run #3	2.915	35.762	200.610
Mean	3.029	36.817	199.705
Std. Dev.	0.099	1.135	4.237
COV (%)	3.255	3.083	2.121

Table 3: Powder dispersed in liquid without riffler

The entire original sample was then placed on the vibrating tray of the spinning riffler. The sample was split into 20 equal sub-samples. Three of the sub-samples were brought to the LA-950 for analysis using the same procedure as described above. The results from these analyses are shown in table 4.

LA-950 WET Analysis with Riffler

Sample Name	D(v, 0.1)	D(v, 0.5)	D(v, 0.9)
Run #1	2.796	36.848	202.660
Run #2	2.828	37.260	205.074
Run #3	2.895	35.998	200.843
Mean	2.840	36.702	202.859
Std. Dev.	0.051	0.644	2.123
COV (%)	1.779	1.753	1.046

Table 4: Powder dispersed in liquid with riffler

Note that the coefficient of variation (COV) decreases for all reported results and now meets the reproducibility expectations set in ISO 13320. The only difference between passing and failing the guidelines was proper sampling.

Suspension sampling

Suspensions may start as a two phase dispersion (particles in liquid or a liquid/liquid emulsion) or be created by dispersing a powder into liquid. Readers interested in the subject of dispersing powders in liquid are directed to ISO 14887 (6) for advice. Regardless of preparation, either a portion or the entire suspension sample must be transferred into the instrument for analysis. If the entire sample is placed in the instrument, then there is no need to consider secondary sampling. But if only a portion of sample is transferred, then secondary sampling needs to be considered.

The most common practice for transferring the sample from the container to the instrument is using a pipette. The unsophisticated practice is to randomly remove a portion and add sample to the instrument until the desired concentration is achieved for analysis. This approach works for easy samples – emulsions or low density particles with a narrow distribution. For example, when working with 1 µm polystyrene latex standards it is almost impossible to not get a representative sample from a beaker into the instrument. But as the density or polydispersity of the sample increases, so does the chance of sampling error during the transfer with the risk being not removing the largest particles. This situation is similar to the powder segregation problem described earlier in this document, but this time with the larger particles sedimenting to the bottom rather than percolating to the top.

ISO 14488 describes two approaches for suspension sampling: splitting by pipette and by multiple capillary tubes. The multiple capillary tubes approach is only used when multiple samples need to be collected and will not be addressed in this document. Almost all suspension sampling performed in the laboratory is done with a pipette. Best practice as suggested in ISO 14488 is to mix the sample in a vessel containing a stirrer and baffles to prevent symmetrical flow. It is suggested to mix the sample thoroughly while

withdrawing the aliquot(s) with a pipette until the desired concentration in the analyzer is reached. This approach is only recommended for samples with particles size < 20-40 µm and without a large variation in density, size, or shape.

Case Study 2

A soil sample was sent to the Irvine, California applications lab for analysis on the LA-950. The standard procedure for soil samples is to first wet the sample in a solution of sodium hexametaphosphate before analysis. The first three measurements shown in table 5 were made using a pipette to transfer the sample from the beaker to the instrument without mixing the sample in the beaker.

LA-950 WET Analysis without Mixing			
Sample Name	D(v, 0.1)	D(v, 0.5)	D(v, 0.9)
Run #1	8.365	43.867	92.267
Run #2	12.596	61.324	113.839
Run #3	14.722	76.164	156.757
Mean	13.659	68.744	135.298
Std. Dev.	1.503	10.493	30.348
COV (%)	11.007	15.264	22.430

Table 5: Soil results from unmixed beaker

A magnetic stir bar was then placed into the beaker and mixed at high rpm. Three more samples were transferred by pipette for analysis. These results are shown in Table 6.

LA-950 WET Analysis with Mixing			
Sample Name	D(v, 0.1)	D(v, 0.5)	D(v, 0.9)
Run #1	11.476	66.064	160.472
Run #2	12.296	65.121	152.838
Run #3	12.722	66.164	156.757
Mean	12.509	65.642	154.798
Std. Dev.	0.301	0.737	2.771
COV (%)	2.409	1.123	1.790

Table 6: Soil results from mixed beaker

The COV values are now within suggested guidelines and the D90 increased with more efficient sampling from the mixed beaker.

Special considerations – toxic samples

This document does not attempt to act as a guide on how to minimize exposure risks to the operator handling particulate materials, but several comments are offered. Follow standard procedures in the laboratory to minimize exposure to toxic materials. Use gloves, a mask if at risk from airborne particles, or perform sample splitting tasks in confined space such as fume hood or containment box.

Conclusions

Sampling is an integral and important component to the overall strategy of generating accurate, reproducible, and meaningful particle size distribution results. The difference between poor and proper results can easily be attributed to poor sampling if not approached with care and understanding. Powders must be mixed, riffled, and handled as discussed in this document in order to minimize errors. Remember that errors in the sampling/analysis procedures impact final product specifications and therefore can have significant economic impact on particulate based products.

References

1. ISO 13320 Particle size analysis – Laser diffraction methods.
2. ISO 14488, Particulate materials -- Sampling and sample splitting for the determination of particulate properties.
3. T. Allen, Particle Size Measurement, 4th ed. Chapman & Hall, London (1993).
4. H. Merkus, Particle Size Measurements; Fundamentals, Practice, Quality, Springer Particle Technology Series, Volume 17, 2009.
5. Photos of samplers courtesy of Restch Technology, see: <http://www.retsch.com/products/assisting/sample-divider/>.
6. ISO 14887, Sample preparation – Dispersing procedures for powders in liquids.