



Solutions in Milling & Sieving

The Art of Milling



AUTHOR

Dr. Andreas Theisen



Team Leader Application Support & Sales Germany



Retsch GmbH
Retsch-Allee 1-5
42781 Haan, Germany

Phone: +49 (0)2104/2333-192
E-mail: a.theisen@retsch.com

www.retsch.com

Representative analysis results require adequate sample preparation

The following situation is typical for many production plants: After a routine quality check, the production process is stopped or an already produced batch is suspended, because the analysis results were not within the relevant critical values. But does the tested product really deviate from the specifications? The quality control managers are convinced of this because modern analysis instruments provide results with very low tolerances. The sample in question was tested several times and the result was confirmed. The question is why the product does not match the specifications although the production parameters have not been changed in any way.

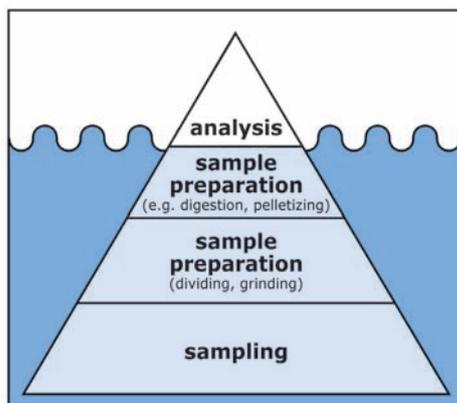


Figure 1: Error pyramid for sample analysis. Analog to an iceberg of which only a small part is visible above the water, only a small part of the actual error sources is perceived during sample analysis.

The possibility that the tested product is indeed deficient cannot be excluded. However, it is often not the product itself which causes irregular analysis results but a lack of understanding of the steps which come before the analysis. Analog to an iceberg which is for the greatest part under water, only a small part of the sum of errors is perceived whereas the major part of potential errors is not taken into account (fig. 1). One reason for this may be that the high accuracy of modern analytical equipment is regarded as the maximum absolute error of the sample preparation process. Another reason may be the fact that sampling and sample preparation are done in a traditional way which has become a routine over the years and is no longer regarded as having a critical influence on the subsequent analyses. Figure 1 demonstrates that the influence of an error in one of the described

steps on the final analysis result can be much bigger than the error which finally occurs during analysis. Moreover, the errors of each step add up, i.e. the error increases during the process (error propagation). The question is now how these errors occur and what can be done to minimize them. In the following, these questions are discussed for the sampling and sample preparation of solids.

Sample handling

In general it can be said that the more heterogeneous a sample, the more important the correct sample preparation. Let's assume that a sample should be taken from a heap of sand. Which sample amount is necessary to represent the properties of the complete heap? Does it matter from which point of the heap the sample is taken? Figure 2 gives answers to both questions: The heap of sand consists of a mixture of bigger stones and smaller sand grains. The stones are found in the upper part, the grains are at the bottom. If, as shown in the picture, a sample is taken only from the upper or lower part of the heap, it consists mostly of stones or grains of sand respectively and is in no way representative of the complete heap. This effect is called segregation and it can be observed when a mixture consists of particles with different sizes or different specific densities. The particle size also has an influence on the sample amount: If 100 g of sample are taken, obviously considerably more sand grains than stones are needed to obtain the required mass. Also less obvious aspects can have an influence here: if the heap of sand was stored outside, then the material on the surface of the heap contains more moisture than the inside part. This means that the property "moisture" is distributed heterogeneously in the initial material. As moist sand weighs more than dry sand, 100 g of sample from the surface of the heap contain fewer sand grains than 100 g of sample taken from inside the heap. In both cases the required sample amount varies due to the properties of the initial material. The required sample amount depends on the distribution range of the properties in the initial material.



Fig. 2: Sampling from a heap of sand

The wider the distribution and the lesser the frequency of properties in a sample are, the more sample material is required. This simple example demonstrates that the sampling and the complete sample handling are strongly influenced by the properties of the initial material. Figure 3 shows the sample handling process. Each step is discussed in the following with regards to its influence on meaningful analysis results.

Sampling

Once determined which properties are to be analyzed, the sample handling process starts with sampling from the initial material. As explained before, it is essential to obtain a representative sample. This means the sample must "represent" all properties of the initial material with statistical security. Consequently, samples in the aforementioned example must be taken from different points in the heap to ensure that the distribution of large and small as well as dry and moist sand grains is fully covered. Moreover, sampling should be free of random error sources which influence the representativeness in a negative way. For many materials the sampling procedure is laid down in DIN standards which also describe the suitable tools. Reproducible results can only be obtained if the sample is representative and if random errors during sample handling have been minimized. This should always be taken into account during each step of the process (see fig. 3).

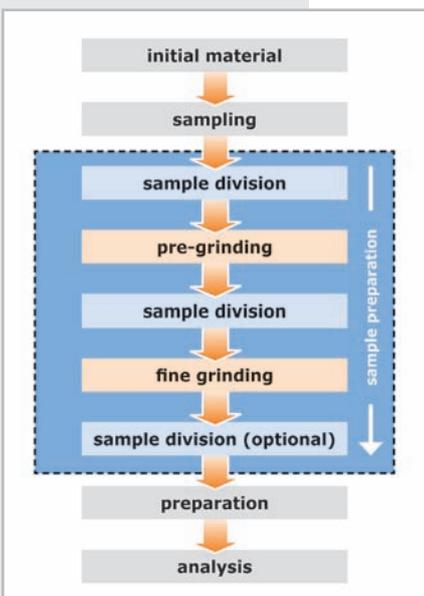


Figure 3: Sample handling step by step

Sample preparation

If a representative sample has been taken, it should have the same properties as the initial material. The sample may show heterogeneously distributed properties as well as segregation effects. During the transport of bulk goods, the larger particles always settle in the upper part of the bulk and the smaller particles at the bottom. That is uncritical if the entire sample is used for analysis. In most cases, however, only a small part of the sample is required so that the volume needs to be reduced. There are two ways to obtain a representative sub-sample: sample division and grinding. Sample division is used to reduce the sample volume. Grinding improves the mixing prop-

erties and homogenizes the sample. A representative sub-sample can also be obtained by combining the three methods, taking into account the product properties and subsequent analysis method. Care must be taken that the properties of the sample are not altered by the preparation process. This can also be explained with our example: if the particle size distribution of the sand sample is to be determined, the sample must not be ground. If the moisture content is analyzed, the sample must not be heated to prevent the contained water from evaporating. In the following the two sample preparation methods are discussed in detail.

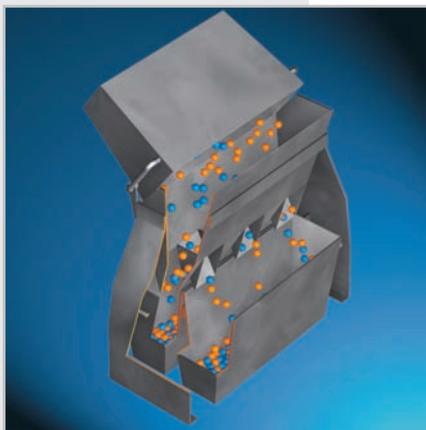


Fig. 4: Functional principle of a sample splitter



Fig. 5: Functional principle of a rotating sample divider



Fig. 6: Functional principle of a rotating tube divider

Sample division

If all properties are distributed evenly in the sample and if there is no segregation, a small part of the sample could be extracted, e.g. with a spoon. However, it is much more common that the properties are distributed heterogeneously or that the exact distribution of the properties is unknown. In such cases, a simple yet representative extraction of a sub-sample is almost impossible. Standardized methods such as the use of sample splitters or rotating sample dividers may be useful. Figure 4 shows the function principle of a sample splitter. The sample splitter is equipped with an even number of equally sized passages which have alternating outlets to the right and left side. The sample is poured from the top into the sample splitter. As all the passages have the same size and each side has the same number of outlets, the sample is split into two equal halves. By further dividing one half, the sub-sample can be further reduced.

In a rotating sample divider, the sample is fed into the hopper and automatically transported via a feed chute to the openings of an evenly rotating dividing head (fig. 5). The sample falls from the end of the chute into the rotating dividing head which divides the sample flow into 6, 8 or 10 sub-samples, depending on the number of outlets. After the division, several sub-samples can be merged or one sub-sample can be further divided.

To divide larger sample amounts, a rotating tube divider is the tool of choice (fig. 6). In contrast to the rotating sample divider, only the feeding tube which transports the sample is rotating. The outlet of this tube rotates over a laboratory bottle which collects the sub-sample. This method is used to extract a sub-sample from the sample flow and not to divide it.

What is the effect of these different dividing methods on the analysis results? As explained at the beginning, reproducible analysis results can only be achieved if the sample is representative of the initial material. This representativeness is considerably influenced by random errors. The sample division method has an influence on the impact of the random error. Random sampling as described in the first part cannot be identically repeated, i.e. the random error has a great impact. With coning and quartering the random error is reduced because a fixed dividing cross is used. However, due to the manual piling of the sample the even distribution of properties within the conical heap cannot be assured. Especially a possible segregation of the laboratory sample during the piling process can have a negative effect. The sample splitter provides better results as the division process is realized by a defined tool. However, the

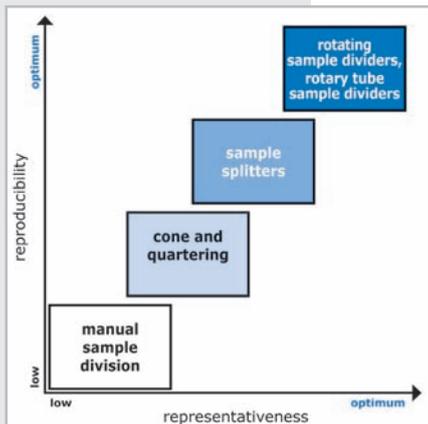


Fig. 7: The reproducibility of analysis results increases with the representativeness of a sub-sample. Automated division methods reduce the probability of random errors thus increasing the representativeness of a sub-sample.

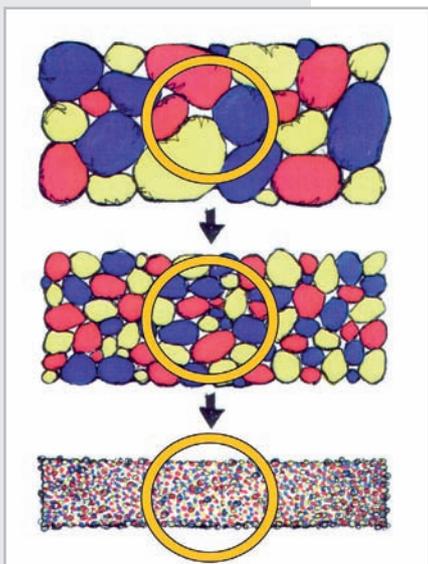


Fig. 8: Grinding means size reduction of a particle collective within the context of representative sample preparation and neutral-to-analysis homogenization

fact that the sample is fed in manually is again a potential source of errors. In rotating sample dividers and rotary tube dividers the sample feeding and the division itself are automated. If the division is carried out with fixed parameters (rotation speed, feeding speed), the sample and thus its properties are evenly distributed into the laboratory bottles. The sub-sample represents the initial sample. If the division is repeated with identical parameters, it provides comparable results so that the analysis is also reproducible. All the described division methods provide better results than manual sample division with a spoon (see figure 7).

Size reduction

Another essential step of sample preparation is size reduction of the sample by grinding. One of the most important rules of thumb for size reduction on a laboratory scale is **to grind the material as fine as necessary**. It is possible to obtain grind sizes below 100 nm for many materials by mechanical grinding, however, the required energy input for producing particles smaller than 50 microns is very high. As our power supply only provides a defined maximum energy it cannot be increased at will. Consequently, grind sizes in the nanometer range can only be achieved with very long grinding times of several hours. For routine tasks in a modern quality control laboratory, sample preparation should not take more than a few minutes. Moreover, long grinding times lead to increased abrasion which could falsify the analysis result. Therefore, it is advisable to consider the question: **which fineness is required to obtain a sample suitable for analysis in the shortest possible time?**

In this context, two aspects of the grinding process should be given special consideration. Firstly, the grinding process serves to homogenize the original material. Secondly, the subsequent sample preparation steps or analysis method may require a certain fineness of the material. We will take a closer look at these aspects in the following paragraph.

I. Homogeneity

For many analysis methods, the amount to be analyzed is only a small fraction of the original material which means that this fraction must represent all the properties of the sample. If you take, for example, a package of muesli to determine the energy value, 1 g of sample has to represent the entire package – including oats, raisins, nuts and dried fruit. No definite particle size has been determined which a sample needs to have to be called homogeneous; however, in practice sizes around 500 microns have been established. Figure 8 shows the effects of grinding graphically. With a particle size of 500 microns and smaller (particle collective at the bottom) it is no longer important where the sample is extracted, the composition is the same for all part samples.

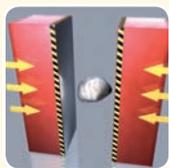


Before grinding



After grinding

SIZE REDUCTION PRINCIPLES

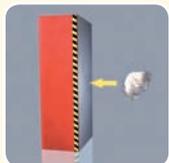


Pressure

Force is applied between two solid surfaces that either represent the grinding tool surfaces directly or may be

the surfaces of adjacent particles. Pressure is exerted by the grinding tools.

Example: jaw crushers

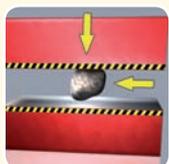


Impact effects

Force at a solid surface. This could either be that of a grinding tool, or be represented by other particles. Strain by impact is

mainly caused by one-sided and opposing particle acceleration.

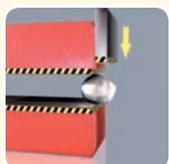
Examples: mixer mills, planetary mills



Friction

Force between two solid surfaces. Caused by the vertical pressure of one surface and the simultaneous movement of the other surface.

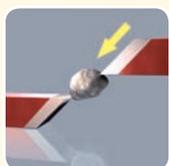
Examples: mortar grinders, disc mills



Cutting

Force between two or more sharp-edged surfaces. There is at least one fixed and one moving cutting edge.

Examples: shredders, cutting mills, knife mills



Shearing

Force between two or more solid surfaces moving in opposing directions which results in a shearing effect. There is at

least one fixed and one moving surface.

Examples: rotor beater mills, cross beater mills, ultra centrifugal mills

II. Analytical fineness

The term "analytical fineness" describes the maximum particle size a sample may have where no systematic error occurs in the subsequent analysis. There are different types of analysis:

- a. **Digestion methods: the solid material is dissolved and burnt before being analyzed.**
 - b. **Extraction methods: the components are extracted or evaporated.**
 - c. **Methods which involve direct analysis of the solid material.**
- a. In case of digestion, the preliminary treatment of the sample is not of importance so that the term "analytical fineness" does not make much sense here. However, care must be taken that the material is not too fine because then the reaction would run too quickly. This is true, for example, of organic samples which oxidize in the presence of nitric acid. If the material is too coarse, the digestion process takes too much time. For these practical reasons, particle sizes around 500 microns are optimal.
 - b. The particle size is of similar relevance for extraction methods. If the powder is too coarse, not everything can be extracted; if the powder is too fine, the extraction thimble is blocked and the material is flushed into the receiver flask. If extraction takes place under pressure, it is recommendable to have particle sizes around 200 microns. The optimum fineness of the sample strongly depends on the extraction apparatus used. For most systems, 500 microns is an ideal size.
 - c. If the material is analyzed directly with a spectroscopic method, the so-called penetration depth is crucial for the required analytical fineness. The penetration depth is the maximum depth from which the electromagnetic ray can exit from the surface. The penetration depth strongly depends on the wave length. In the case of NMR spectroscopy, the penetration depth lies in the meter range. For NIR analyses it is about 1 cm and for X-rays in a range around 100 microns. It can generally be said that with decreasing wave length, the penetration depth decreases as well. Therefore, the particle size for NIR analysis should be around 500 microns to ensure that the ray of light completely penetrates the particles. For XRF analysis the particle sizes should be below 100 microns to guarantee complete penetration.

In summary, it can be said that size reduction of samples down to 500 microns is sufficient for most analysis methods – with regards to homogeneity as well as analytical fineness. For extraction under pressure, the sample may also be finer. Only for **XRF methods** it is essential to obtain **particle sizes below 100 microns**.

RETSCH offers a great variety of crushers and mills for the size reduction and homogenization of solids for subsequent analysis. Depending on the mill, different size reduction principles are applied to grind the sample down to the desired fineness (see figure 10). Hard-brittle materials, for example, are best comminuted with impact and friction whereas for soft and elastic materials, size reduction with knife or cutting mills is the most suitable method. In general, pulverization to sizes below 50 μm can only be effected with friction. To make laboratory mills suitable for a wide range of applications, different size reduction principles are combined in one mill – for example pressure and friction in mortar grinders.

Figure 10: Different size reduction principles

Grinding tools

The selection of suitable grinding tools is an important aspect of neutral-to-analysis sample preparation, as the following examples show:

- If a soil sample is to be analyzed for its calcium, silicon oxide or cobalt contents, it must not be processed with grinding tools of stainless steel or hardened steel, as these steels contain the elements to be analyzed.
- Cement clinker, in contrast, can be ground with grinding tools of these materials if the calcium and silicon oxide content is to be determined.
- PTFE, zirconium oxide and glass are materials which can be sterilized and are therefore frequently used for applications in the food chemistry and microbiology sector.
- The hardness of the sample material needs to be considered, too. Corundum, for example, cannot be ground with agate grinding balls.

The “**art of milling**” consists in preparing a laboratory sample in such a way that the result is a **representative individual sample** with **homogeneous analytical fineness**. When selecting a suitable mill and grinding tools, care must be taken that the sample properties to be analyzed (e.g. moisture content, heavy metal content etc.) are not altered during the process in any way. In addition to a profound knowledge of the grinding instruments, experience in preparing a variety of different materials is required. It is therefore essential to either fall back on practical experience or to do some test grindings before purchasing a laboratory mill.



CONCLUSION

A faultless and comparable analysis is closely linked to an accurate sample handling. Only a sample representative of the initial material can provide meaningful analysis results. Rotating dividers and rotary tube dividers are an important means to ensure the representativeness of a sample and thus the reproducibility of the analysis. Correct sample handling consequently minimizes the probability of a production stop due to incorrect analysis results as described at the beginning of this article. Thus correct sample handling is the key to effective quality control.