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Technical Note

# Principles of Sample Preparation by Grinding or Comminution

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## Introduction

Sample preparation is the process where a representative piece of material, chemical or substance is extracted from a larger amount, bulk or batch for subsequent analysis. Representative samples are selected to accurately reflect the larger group and represent the characteristics of the whole material. Ideally representative samples are homogeneous or similar in nature, but when that is not possible, the best attempts must be made to achieve samples which represent the majority of the characteristics of the larger grouping.

The preparation of samples is one of the most important steps in analytical methods for many reasons, including the fact that some materials cannot be analyzed in an in-situ condition (such as proteins, DNA and RNA). Some samples have interfering substances and species that can produce faulty results. Sample preparation can include many processes, from reactions or treatment with chemical agents, to filtration, dilution, and extraction.

## Particles and Homogeneity

Many physical samples need particle size reduction to create representative samples, usually due to their overall heterogeneous nature or state when laboratory or testing samples require a certain level of homogeneity. Homogeneity is the state of being of uniform composition or character, whereas heterogeneity lacks uniformity in one or more characteristics. Homogeneity and heterogeneity often depend on perspective and context where the smaller the sampling frame, the less homogeneous a material or substance can appear. For some samples, the measure of homogeneity can be accomplished with a process that creates large size reduction (crushing) where other samples for other processes will require reduction to fine particles (milling). Smaller particles and homogeneous materials are most often needed for many further laboratory sample preparation techniques.

Laboratory or analytical samples must be processed into a form which allows for extraction or digestion ultimately for an analytical instrument or chemical testing. Sample processing involves reducing the material size to ensure samples for homogeneity and extraction into a suitable matrix for analysis. The most common method for obtaining a homogeneous sample is grinding or comminution. Grinding samples allows for a reduced sample size in order to increase accuracy and decrease uncertainty. In a study by Thiex et al., it was shown that the smaller the particle size, the less sample was needed to achieve a lower amount of uncertainty in a sample (Table 1).

Table 1. Effect of particle size on amount of material, in grams, needed to ensure various uncertainty levels for representative samples.

| | 15% | 10% | 5% | 1% |
|---|---|---|---|---|
| 5 mm | 56 | 125 | 500 | 12,500 |
| 2 mm | 4 | 8 | 32 | 400 |
| 1 mm | 0.4 | 1 | 4 | 100 |
| 0.5 mm | 0.1 | 0.1 | 0.5 | 12.5 |

## Principles of Particle Reduction

The most common method for obtaining a homogeneous sample is grinding of comminution. Grinding samples has many benefits for sample preparation since it increases homogeneity, increases surface area and decreases particle size which can improve extraction efficiency. Some of the negatives regarding grinding samples are: potential contamination, increase in moisture, evaporation, loss or alteration of volatile compounds or labile constituents, and safety issues regarding grinding.

Sample size reduction is accomplished by either crushing or grinding using forces of impact, attrition, shearing, or compression (Figure 1).

- **Impact Force**: the striking of one object or material against another. One object may either be stationary or both may be in motion.
- **Attrition Force**: created by materials rubbing against each other usually in opposite directions or planes.
- **Shearing force**: cleaving or cutting of a material by some cutting implement or blade.
- **Compression force**: slow application of a force against a solid to crush it into smaller pieces usually between two solid surfaces.

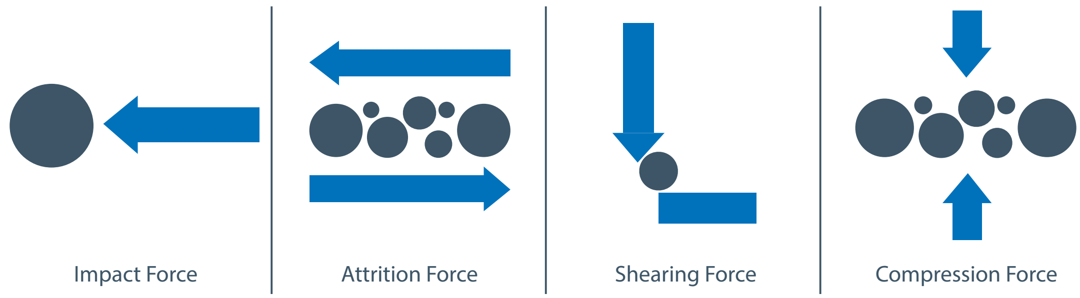


Figure 1. Grinding forces.

Particle reduction of solids occurs in multiple stages starting with the accumulation of defects or stresses in a concentrated location increasing the strain on a solid or particle. The stress forms microcracks and in crystal lattices, it will disrupt the crystal lattice in several cells or locations. The microcracks then join to form a larger major disruption or crack which ultimately divides the solid into pieces (Figure 2).

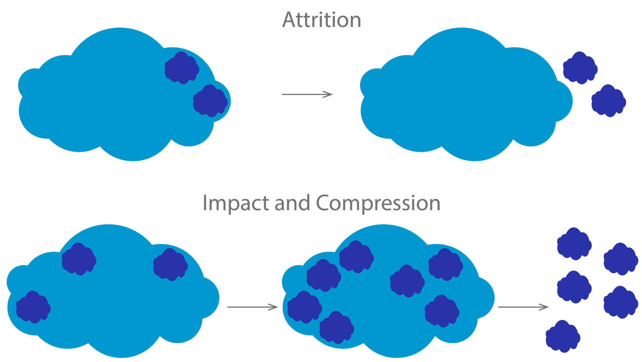


Figure 2. **Attrition**: Smaller particles break off larger particles through rubbing against a surface or each other. **Impact and Compression**: Faults or microcracks within larger particles increase with increasing force causing the larger particle to break apart.

Different applications, quantity of throughput and final end products often designate the method employed to grind materials (Figure 3). Crushers are commonly shearing or compression disruptors and are used to create larger particles in the 50-100 mm range. These particles are often just a primary step in some processing schemes. Most crushers are able to either process a large continuous stream of materials or larger batches. Grinders often produce smaller particles in smaller scales. There are many types of grinders based on the method of grinding and the force used to grind materials.

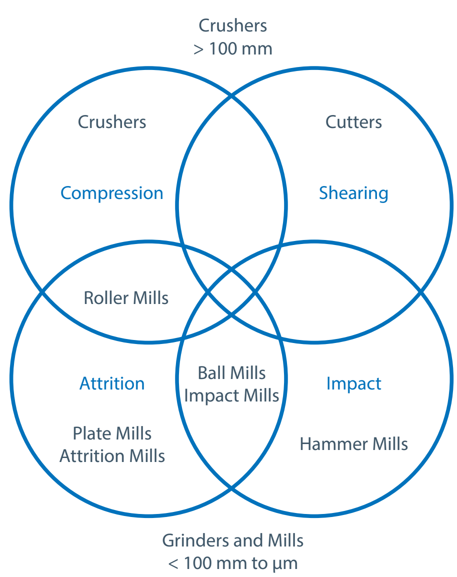


Figure 3. Types of crushing and grinding machinery for laboratory use.

Different applications, quantity of throughput and size of final products often designate the method employed to grind materials from large scale crushers to finer impact mills. Table 2 gives the relative reduction of particle size from original material and the equipment needed.

Table 2. Particle size reduction comparison table.

| Particle Size | Reduction from Original | Type of Equipment |
|---|---|---|
| Large | 2-5 x | Crusher |
| Medium | 5-10 x | Crusher |
| Fine | 10-50 x | Crusher or Mill |
| Microfine | 50-100 x | Mill |
| Superfine | 100-1000 x | Mill |

Mills are the most common laboratory grinders used to create fine, microfine or superfine particles needed for analytical testing and processing. Some common laboratory mills include (Figure 4):

- **Ring and Puck Mills** use multiple grinding surfaces usually as opposing plates that move in opposite directions with a disc or puck moving and grinding materials on a plane.
- **Impact Mills** have a moving impactor that pulverizes a sample through repetitive motions.
- **Ball Mills or Ball-Medium Mills** grind through impact of a grinding media such as balls, rods, etc.
- **Vibratory or Shaker Mills** use high speed vibrations and grinding media to combine multiple grinding forces to reduce materials to fine powders. These mills can include grinding forces and media like balls, beads and grinding media.
- **Combination Mills** use multiple techniques and forces such as combination of ball media with vibratory and shaking motions


Shatterbox Freezer/Mill Mixer/Mill Geno/Grinder

Figure 4. Examples of Ring/Puck Mill, Impact Mill, Ball Mill, and Combination Mill from Cole-Parmer.

## Understanding Material State

The selection of the correct type of mill depends on the material and the factors that will affect size reduction. The most important factors that must be considered when selecting a grinding method are:

- **Hardness or toughness:** particularly hard samples will need energy intensive grinding methods such as crushers or cutters.
- **Material structure**: samples that are abrasive will cause wear of the grinding system and cause higher amounts of contamination. Sticky samples can clog grinding heads and screens. Low density samples or powders may not enter the grinding media area or float above the grinding surfaces.
- **Moisture content**: samples with more moisture are harder to grind and cause more clogging of the systems. High moisture samples are more often ground in ball medium type mills or closed systems without filters or screens.

- **Melting or softening temperature**: grinding generates energy and heat which can cause material to soften or melt which can degrade samples or volatilize organic compounds. In the thermally labile products or samples sometimes additional cooling of the material or grinding system is needed to prevent sample loss or promote efficient grinding.
- **Purity of required material**: grinding methods often create exposure to other materials of the grinding system or other previously ground materials.

The most efficient grinding system is a system that applies the minimum amount of energy to rupture the material without adding excess energy or heat. Energy is required to reduce particle size, but it also generates heat which can change the sample state or degrade materials. It also then applies that ability to reduce heat generation or negate the effects of heat on the grinding system that allows for application of more energy into the system to create a more efficient particle reduction.

## Energy and Particle Reduction

The energy involved in grinding and size reduction is not particularly efficient with only a small amount of the energy being used to increase surface area and initiate flaws and cracks in particles. The majority of the energy is: friction within the grinder between surfaces, media and material; heat, vibration and noise.

There are three primary theories for the science of size reduction that include: Rittinger's Law, Kick's Law and Bond's Law. Rittinger's Law was based on the assumption that particles do not deform before breaking and are therefore infinitely brittle. This law states that the energy required for size reduction of a unit of mass is proportional to the new surface area produced (Figure 5). Rittinger's Law is best when there is a large size difference between the coarse material and the fine resulting particles.

$$E = K_R \left( \frac{1}{d_2} - \frac{1}{d_1} \right) \quad \text{or} \quad E = K_R (S_n - S_i)$$

E = Energy required per mass of material being ground
$K_R$ = Rittinger's constant
$d_1$ = Average size of initial pieces ($1/d_1 = s_i$); $s_i$ = initial surface area
$d_2$ = Average size of ground particles ($1/d_2 = s_n$); $s_n$ = ground surface area

Figure 5. Rittinger's Law

The second theory of particle reduction is Kick's Law which is more accurate for coarse crushing where most of the energy is used to cause fractures to appear in existing cracks and deformities. This law applies best when the difference between the size of the coarse material and the final size of the particle is quite large. The energy into the system is proportional to the size reduction ratio, meaning that the energy need for a 1000 x size reduction is the same whether it is between materials starting at centimeter or microns (Figure 6).

$$E = K_K \ln \left( \frac{d_1}{d_2} \right)$$

E = Energy required per mass of material being ground
$K_K$ = Kick's constant
$d_1$ = Average size of initial pieces
$d_2$ = Average size of ground particles
d1/d2 = Size reduction ration (RR)
Fine grinding RR =/> 100:1
Coarse grinding RR =/< 8:1

Figure 6. Kick's Law

The final theory of particle reduction is Bond's Law that states the total work input by the weight of crushed material is inversely proportional to the square root of the diameter of the product particles (Figure 7). Bond's Law functions best in between the coarse grinding of Bond's Law and the fine grinding of Rittinger's Law.

$$\frac{E}{W} = \sqrt{\frac{100}{d_2}} - \sqrt{\frac{100}{d_1}}$$

E = Energy required per mass of material being ground
W = Bond Work Index required to reduce a unit of weight
$d_1$ = Average size of initial pieces
$d_2$ = Average size of ground particles

Figure 7. Bond's Law

## Conclusions

The selection of a laboratory grinding apparatus depends on a number of factors from the type of material and its properties to the final state of the samples to be produced. Cole-Parmer has a wide range of products that can fit all of your sample processing needs.

## Decision Flow Chart

**What Type Of Sample Preparation Do You Need?**