MILLING SIEVING ASSISTING

the sample

Verder Scientific Customer Magazine | Issue 44

part of VERDER scientific

BALL MILLS

FROM NANO GRINDING TO MECHANOCHEMICAL SYNTHESIS

RETSCH introduces the first mixer mill on the market to achieve grind sizes in the nanometer range.

Mixer Mill MM 500

www.retsch.com/mm500

Dear Readers, Customers and Business Partners,

Ball mills are among the most variable and effective tools when it comes to size reduction of hard, brittle or fibrous materials. The variety of grinding modes, usable volumes and available grinding tool materials makes these mills perfectly suited for a vast range of applications – from producing nanosized particles to effecting mechanochemical synthesis of two or more materials.

That is why RETSCH has developed the widest range of ball mills in the world. On the following pages you will not only read about the different types and models but will also gain insight into application specifics like correct ball fillings or how to go about achieving a particular grind size.

Our latest addition to the ball mill range is the Mixer Mill MM 500. This mill is unique as it combines the ease of use of a classic mixer mill with the power and performance of a planetary ball mill. Thanks to a frequency of 35 Hz the MM 500 generates enough crushing power to produce particles in the nanometer range - a unique feature which no other mixer mill in the market offers.

We hope you enjoy reading this issue of "the sample"!

Your

Dr. Juergen Pankratz
CEO Verder Scientific

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Content
BALL MILLS

Visit www.retsch.com/downloads to view a recording of the **WEBINAR "USEFUL TIPS FOR EFFICIENT GRINDING PROCESSES IN LABORATORY BALL MILLS"** or download our white paper on efficient ball milling.

MECHANOCHEMISTRY IN BALL MILLS

In the light of sustainability and Green Chemistry, mechanochemistry offers fast reactions in a solvent-free environment. Mass productivities often exceed the solvent-based reaction equivalents and the work-up procedures are generally easier. Hence, mechanochemistry may become the cornerstone of sustainable energy in the future.

In chemistry one often classifies a reaction based on the way the energy is supplied. Consequently, the best-known types of reactions are thermal (energy supplied by heating), electrochemical (energy supplied by electrical current) and photochemical (energy supplied by optical waves). A less known form of chemistry is mechanochemistry where the energy is supplied by impact and shearing forces.

The 21st century brought with it a growing consciousness of the environmental impact of chemical reactions and chemists started to examine alternatives to solvents, some of them trying to avoid them altogether. Thus, mechanochemistry slowly gained momentum in disciplines like organic chemistry where it was quickly shown that staple reactions like C-C couplings, oxidations, reductions and pericyclic reactions can be transferred into ball mills. Unlike the mortars used in former times, ball mills allow for precise control of the reaction conditions, a wide range of different energy inputs and the possibility to conduct reactions in sealed vessels. **Mills typically used for these reactions are planetary ball mills and mixer mills with grinding jars ranging from 2 ml up to 500 ml.** The ball size is critical because the balls themselves initiate the reaction and have to create a new reactive surface by removing the reacted layer. If the balls are too small, the energy supplied is insufficient and the balls also tend to agglomerate. If the balls are too big, reactions are initiated but the amount of reactive collisions is rather small and the reaction product is not efficiently removed from the particle surface, leading to small reaction rates. Suitable balls therefore range from 5 to 15 mm in diameter, offering a good compromise. The jar and ball materials are also very crucial in mechanochemical applications. The material, such as zirconium oxide or stainless steel, must be resistant to the chemicals while being mechanically stable to avoid excessive abrasion.

HOW DOES MECHANOCHEMISTRY WORK?

For mechanochemistry, the mode of energy impact seems to play a vital role. Whereas in planetary ball mills shearing is the predominant size reduction principle, it is impact in mixer mills. Beside the type of mill, scientists had to re-evaluate parameters of "classical" chemical reactions, like concentration and temperature, when transferred to a ball mill, as these are different in the solvent-free environment. Interesting results have been presented by the group of Stuart James [1]. They conducted a chemical reaction at different temperatures and milling frequencies and showed that only the frequency has an influence on the kinetics of the reaction (Fig. 1) while an increase in temperature had no effect.

[1] Ma, X., Yuan, W., Bell, S. E., & James, S. L. (2014). Better understanding of mechanochemical reactions: Raman monitoring reveals surprisingly simple 'pseudo-fluid' model for a ball milling reaction. Chemical Communications, 50(13), 1585-1587.

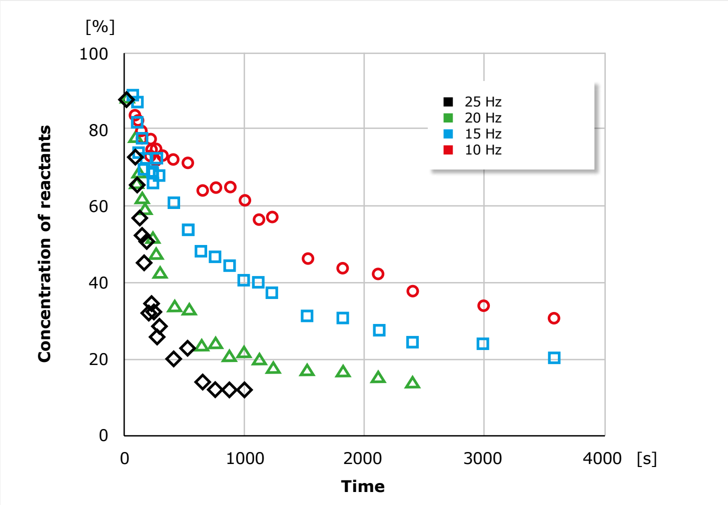


Fig. 1: The rate of reaction shown as unreacted reactant against time at an energy input varying from 10 to 25 Hz in the Mixer Mill MM 400. The rate of reaction increases with the frequency.

Author: Dr. Sven Grätz, postdoctoral research associate, Ruhr University Bochum, Germany, Faculty of Chemistry and Biochemistry, Chair in Inorganic Chemistry I, Prof. Borchardt

THE PERFECT BALL MILL FOR EVERY APPLICATION

The RETSCH ball mill range is the most extensive offering in the world, providing a high degree of flexibility. The portfolio comprises mixer mills, planetary ball mills, high energy ball mills, XRD mills, and drum mills. Whereas the mixer mills are used for dry/wet/cryogenic grinding and homogenizing small sample volumes, the planetary ball mills meet and exceed all requirements for fast and reproducible grinding of larger volumes down to the submicron range as well as mechanical alloying. The High Energy Ball Mill Emax and the Mixer Mill MM 500 provide grind sizes in the nanometer range in a very short time and are also used for mechanical alloying and mechanochemical applications. The XRD-Mill preserves the crystalline structure of the sample for subsequent XRD analysis. The Drum Mill TM 300 with its ball and rod modules is used for fine grinding of solid matter by impact and friction, in wet or dry condition. Whatever your requirements may be **– RETSCH has the perfect ball mill for your application!**

WIDEST RANGE OF BALL MILLS WORLDWIDE	Mixer Mill MM 200	Mixer Mill MM 400	Mixer Mill MM 500
			
Max. sample volume	2 x 10 ml	2 x 20 ml	2 x 45 ml
Available grinding tool materials	6	6	4
Dry grinding	✓	✓	✓
Wet grinding	–	●	✓
Cryogenic grinding	–	✓	✓
Nano grinding	–	–	✓
Bead beating	✓	✓	–
Mechanochemical processes	–	✓	✓
Continuous cooling (with 5 °C cold water)	–	–	–
Continuous cooling at -196 °C with LN_2)	–	–	–
High-impact pulverization (with 1 large ball)	✓	✓	✓
Time required to produce nano particles	–	–	fast
Long-term grinding **(continuous)**	– –	– –	✓ ✓
Gentle grinding with low energy input	–	–	–
Preservation of crystal sample structure	●	●	●
Jars pressure-tight < 5 bar	–	●	✓
Jars with integrated safety closure	–	–	✓
Jars stay clamped in the mill for sub-sampling	–	–	✓
Legend: ✓ Suitable | – Not suitable | ● Suitable to a limited extent		see page 14	see page 6

- DRY GRINDING
- WET GRINDING
- CRYOGENIC GRINDING
- NANO GRINDING
- BEAD BEATING
- MECHANOCHEMISTRY
- MIXING

CryoMill	Planetary Ball Mills PM 100/200/400	High Energy Ball Mill Emax	XRD Mill McCrone	Drum Mill TM 300
				
1 x 20 ml	1 x 220 ml / 2 x 50 ml / 4 x 220 ml	2 x 45 ml	1 x 4 ml	1 x 20 l
4	7	3	3	2
✓	✓	✓	✓	✓
✓	✓	✓	✓	✓
✓	●	–	–	–
–	✓	✓	–	–
–	–	–	–	–
–	✓	✓	–	–
–	–	✓	–	–
✓	–	–	–	–
✓	–	–	–	–
–	moderate	very fast	–	–
– –	✓ –	✓ ✓	✓ ✓	✓ ✓
–	✓	–	✓	✓
●	–	–	✓	–
●	●	✓	–	–
–	–	✓	–	–
–	–	–	–	–
see page 10	see page 18	see page 20	see page 22	see page 23

RE-INVENTING BALL MILL TECHNOLOGY

MIXER MILL MM 500

NEW

- DRY GRINDING
- WET GRINDING
- CRYOGENIC GRINDING
- NANO GRINDING
- MECHANOCHEMISTRY
- MIXING

THE POWER OF A PLANETARY BALL MILL COMBINED WITH THE CONVENIENCE OF A MIXER MILL

With the new Mixer Mill MM 500 RETSCH has developed the perfect combination of a classic mixer mill and a planetary ball mill. Thanks to a maximum frequency of 35 Hz, the MM 500 is the first mixer mill in the market with sufficient energy input to generate particles in the nanometer range without requiring cooling breaks.

So far, planetary ball mills have been the instrument of choice for long-term grindings with high energy input aiming to obtain particles sizes < 1 µm, e. g. **for mechanical alloying or chemical reactions**. Despite their benefits for this type of application, their major drawback is requiring cooling breaks and that they are not as easy to handle as mixer mills. The new MM 500 now fills this gap. With **jar volumes up to 125 ml** and with its suitability for **long-term grinding processes up to 99 hours,** it is a real alternative to planetary ball mills with more **comfortable handling** and **less warming effects.**

THE TWO GRINDING MODES: HIGH IMPACT VERSUS HIGH FRICTION

The number and size of the grinding balls used in the MM 500 determine the predominant grinding mechanism: one large, heavy grinding ball leads to **high-impact mode,** i.e. the ball with its elevated mass hits the rounded ends of the jar with high impact. This mode is the best option for quick pulverization processes where the sample does not have to be ground to the finest possible size. It is also the method of choice for larger initial feed sizes, as the grinding ball must be three times bigger than the biggest particle. Another strong advantage is the ease of handling if just one grinding ball is involved. The high-impact mode is unique to mixer mills and is intensified in the MM 500 by the high frequency of 35 Hz (2100 min^{-1}).

Using several balls with smaller diameters generates intense friction between grinding balls, jar walls and sample material. This **high-friction mode** produces very fine particle sizes and is typical for planetary ball mills; it is also beneficial for milling fibrous samples. In contrast to planetary ball mills, high-friction mode causes less warming in mixer mills due to the different ball movement.

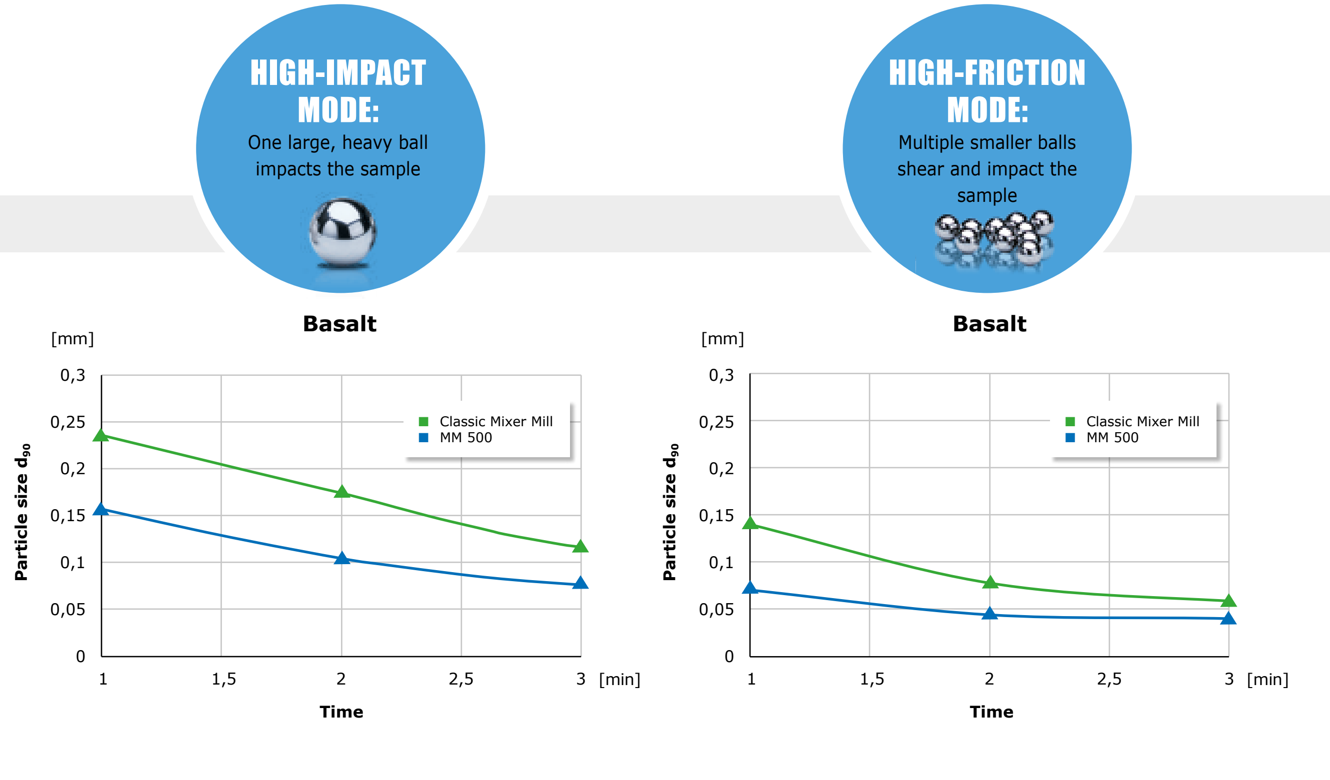


Fig. 1: Grinding of basalt in the MM 500 and a classic mixer mill in different modes.

Left: High-impact mode with one large and heavy ball. The MM 500's higher energy input of 35 Hz leads to **1.5 x finer grinding results** compared to the classic mixer mill with 30 Hz. The high-impact mode delivers similar results in the 80 ml jar of the MM 500 but not in the 125 ml jar, as the single ball has too much room and does not impact on the sample with the required frequency.

Right: The high-friction mode with several smaller balls produces finer particle sizes and delivers similar results for all three jar volumes. Again, 35 Hz lead to a better final fineness than 30 Hz.

NANO GRINDING WITHOUT COOLING BREAKS

While the MM 500 fulfils all the requirements of a classic mixer mill for fast pulverization of soft, elastic, fibrous, hard and brittle samples in dry, wet or cryogenic mode, it stands out from the rest due to its suitability for new types of applications, These include colloidal grinding of samples down to < 100 nm but also mechanochemical applications, not possible with a mixer mill so far.

When samples need to be pulverized over a longer period of time to obtain particle sizes in the nanometer range, the MM 500 allows for substantial time savings compared to planetary ball mills due to the fact that it can be operated without cooling breaks; this is a significant advantage over planetary ball mills which generate too much heat to be operated without interruptions.

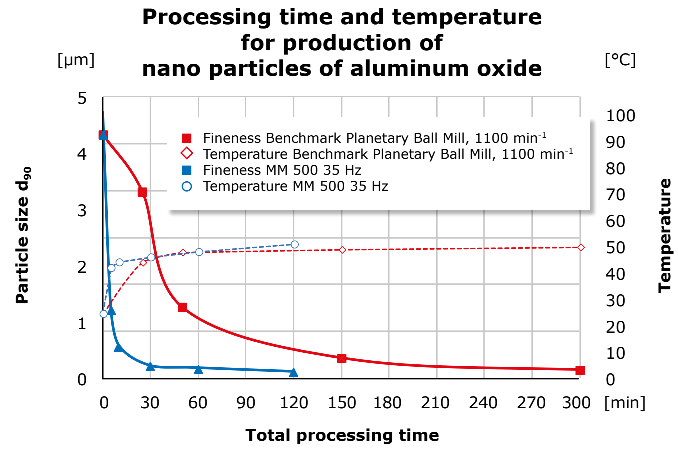


Fig. 2 shows the development of particle fineness and temperature during wet grinding. The MM 500 was operated without cooling breaks, the total process time therefore equals the net grinding time. The MM 500 produced particles of 0.14 µm within 2 h net grinding time, whereas 5 h total process time including cooling breaks (1 h net grinding) were required in the Benchmark Planetary Ball Mill to obtain a particle size of 0.18 µm.

Fig. 3: The innovative Screw-Lock grinding jars are easy to handle and clamping is a matter of seconds. The jars remain clamped in the mill for extraction of a sub-sample or a quick visual check of the sample

OPERATING CONVENIENCE 2.0

The MM 500 provides maximum operational convenience. The user can store up to 12 standard operation procedures (SOPs) via the large 4.3-inch touch display. Grinding processes > 8 h can be realized by using **program cycles of which 4 may be stored**. Here, two parameter sets are combined and repeated up to 99 times, increasing the total processing time up to 99 h. With the new optional RETSCH App, the user can control the mill via smart phone or tablet, create application routines, access the RETSCH application database or get in touch with the RETSCH service team.

The **innovative Screw-Lock grinding jars**, which are pressure-tight up to 5 bar, are safe and easy to handle. The lid is simply screwed tight and the jar is inserted in the clamping system; it may even remain there for extraction of a sub-sample or a quick visual check. The clamping procedure is more user-friendly compared to other ball mills.

EXAMPLE: CRYOGENIC GRINDING OF RUBBER

8 MM INITIAL SIZE

0.7 MM FINAL FINENESS

For cryogenic applications, where the sample is embrittled with liquid nitrogen to improve its breaking behavior, the MM 500 produces better final fineness compared to classic mixer mills with 30 Hz. Another advantage of the MM 500 are the larger jar sizes allowing for more sample quantity compared to those used in other mixer mills.

Example: Cryogenic grinding of rubber granulate in the MM 500 for 8 min with intermediate cooling every 2 min. Compared to the results in a mixer mill with 30 Hz, the particles are 40 % finer.

SCREW-LOCK GRINDING JARS ALLOW FOR USE OF FULL VOLUME

The jar design ensures optimum utilization of the usable volume (Fig. 4). This is an advantage over the jars of classic mixer mills where the lid forms part of the jar volume (Fig. 5). Filling 60 % of the jar with balls plus sample and liquid, as is required for wet grinding, is very hard to achieve in these jars. Moreover, it is more convenient for the user to fill in fibrous sample materials when the jar volume is not part of the lid.


❹ Screw-Lock grinding jar for MM 500


❺ Standard grinding jar for MM 400

❹ **FLAT LID, 0 % VOLUME; 100 % VOLUME IN THE JAR**
→ Fill in "enough" fibrous sample ✓
→ 60 % balls for wet grinding + sample + liquid ✓

❺ **33 % VOLUME IN THE LID; 67 % VOLUME IN THE JAR**
→ Fibrous sample spills over
→ 60 % balls for wet grinding + sample + liquid ✗ not possible

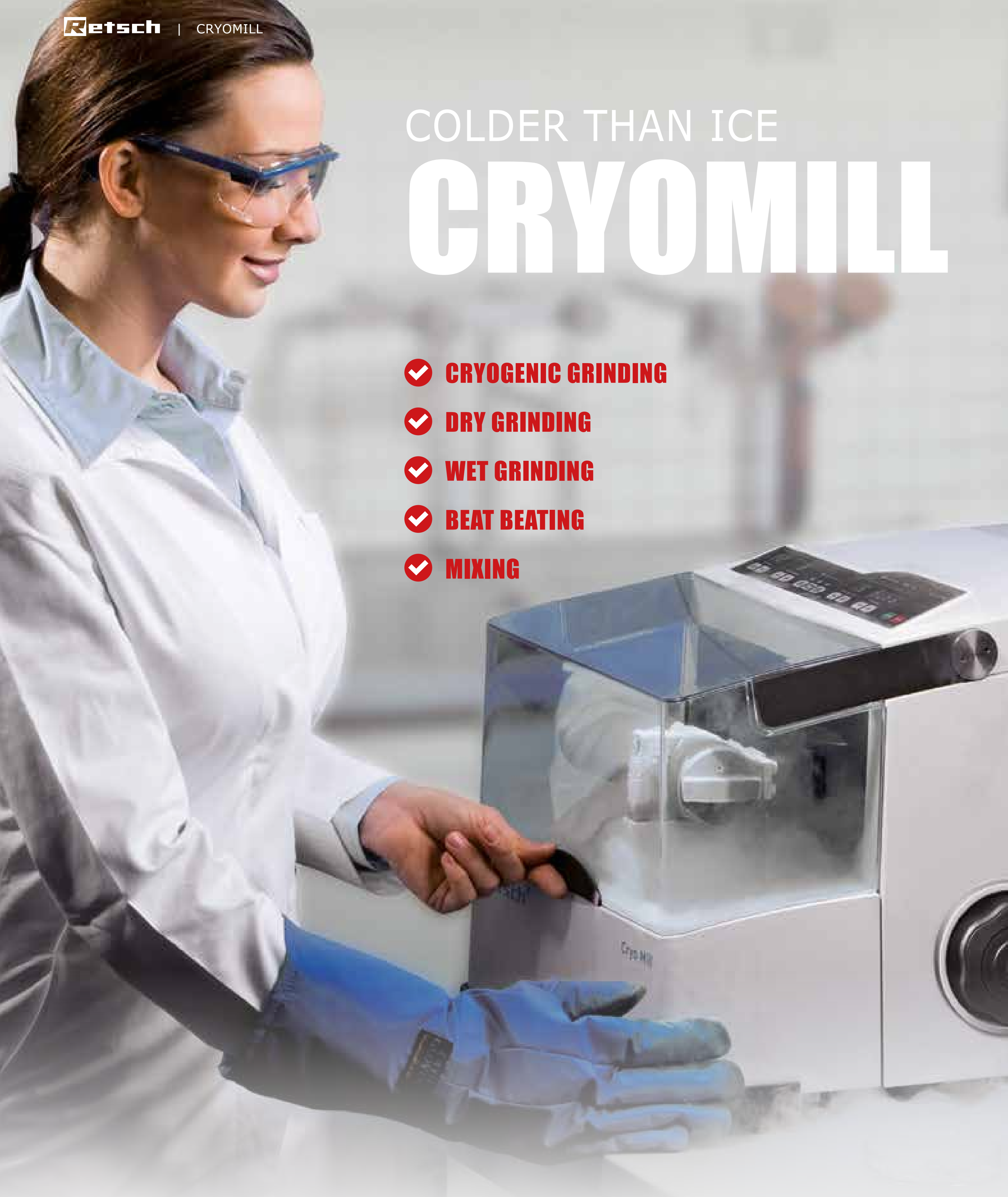

Fig. 6: The Screw-Lock grinding jars are available in 4 different materials

RANGE OF SCREW-LOCK GRINDING JARS

Volume [ml]	Stainless steel	Hardened steel	Zirconium oxide	Tungsten carbide
50	✓	✓	✓	✓
80	✓	✓	✓	✓
125	✓	✓	✓	

IN A NUTSHELL

The new MM 500 is the perfect combination of a classic mixer mill and a planetary ball mill. On the one hand, it achieves excellent grinding results within a few minutes, on the other hand, it is powerful and robust enough to carry out long-term grindings in the nanometer range or mechanochemical processes. On top of that, uncomplicated handling ensures safe operation.



COLDER THAN ICE

CRYOMILL

- CRYOGENIC GRINDING
- DRY GRINDING
- WET GRINDING
- BEAT BEATING
- MIXING

Not all sample materials can be pulverized at room temperature. For ductile and elastic materials cryogenic grinding is the only way to achieve the grind sizes required for subsequent analysis. Through cooling with liquid nitrogen to -196 °C, the sample material is embrittled to break more easily. Moreover, volatile substances are preserved and can thus be quantified. Thermally induced degradation is further prevented by cooling the sample before and during grinding. RETSCH's CryoMill is the perfect solution for grinding these samples efficiently and safely.

AUTOFILL SYSTEM ENSURES USER SAFETY

One particular advantage of the CryoMill is the high operating safety, as the user never comes in contact with the liquid nitrogen. The supply from the integrated Autofill system is controlled by a temperature sensor so that LN_2 is always provided in the exact amount that is needed to keep the temperature at -196 °C. The automatic cooling system guarantees that the grinding process will not start before the sample is thoroughly cooled – this reduces consumption and guarantees reproducible grinding results. With a frequency of 30 Hz, the mill grinds a variety of materials very effectively within a few minutes.

In order to ensure the best possible adaptation to different samples, pre-cooling, grinding time, and intervals are freely programmable. During pre-cooling or interval times, the grinding jar is slowly moved at 5 Hz, keeping the grinding ball permanently in motion to prevent it from freezing and sticking in humid samples.

APPLICATION EXAMPLES CRYOMILL

Sample	Grinding jar size	Grinding ball size	Material	Sample amount	Grinding time	Final fineness
Rubber	50 ml	1 x 25 mm	stainless steel	6 g	2 min	< 400 µm
Textile	50 ml	1 x 25 mm	stainless steel	2 g	4 min	< 500 µm
Hair	25 ml	6 x 10 mm	stainless steel	1 g	4 min	< 200 µm
PET Granulate	50 ml	1 x 25 mm	stainless steel	3 g	4 min	< 300 µm

EXAMPLE: CRYOGENIC GRINDING OF PVC

Diethylhexyl phthalate (DEHP) is widely used as a softener to make polyvinylchloride (PVC) more flexible. PVC can be found, for example, in cable sheathing or PVC hoses. In products like children's toys, however, its use is forbidden as it is regarded to have a harmful effect on fertility and is classified as cancerogenic. Many products potentially containing DEHP or other critical softeners need to be analyzed. Prior to analysis, a one- or two-step sample preparation is required, depending on whether the sample size calls for pre-cutting.

Larger samples of PVC can be pre-cut in a Cutting Mill SM 300 using a 6-disc or a parallel-section rotor and a 6 mm bottom sieve. The granulate resulting from this step can now be pulverized in the CryoMill. Usually, the 50 ml stainless steel grinding jar with one large 25 mm grinding ball, also stainless steel, is suitable to grind about 6 g plastic material. After automatic pre-cooling the sample is pulverized in 9 x 3 min to a final size d_{90} = 200 µm.

❶ PVC SAMPLE

❷ AFTER PRE-CUTTING IN A CUTTING MILL SM 300

❸ PULVERIZATION IN THE CRYOMILL TO 200 µM

HOW TO ASCERTAIN CORRECT JAR FILLINGS AND BALL SIZES FOR SUCCESSFUL BALL MILLING

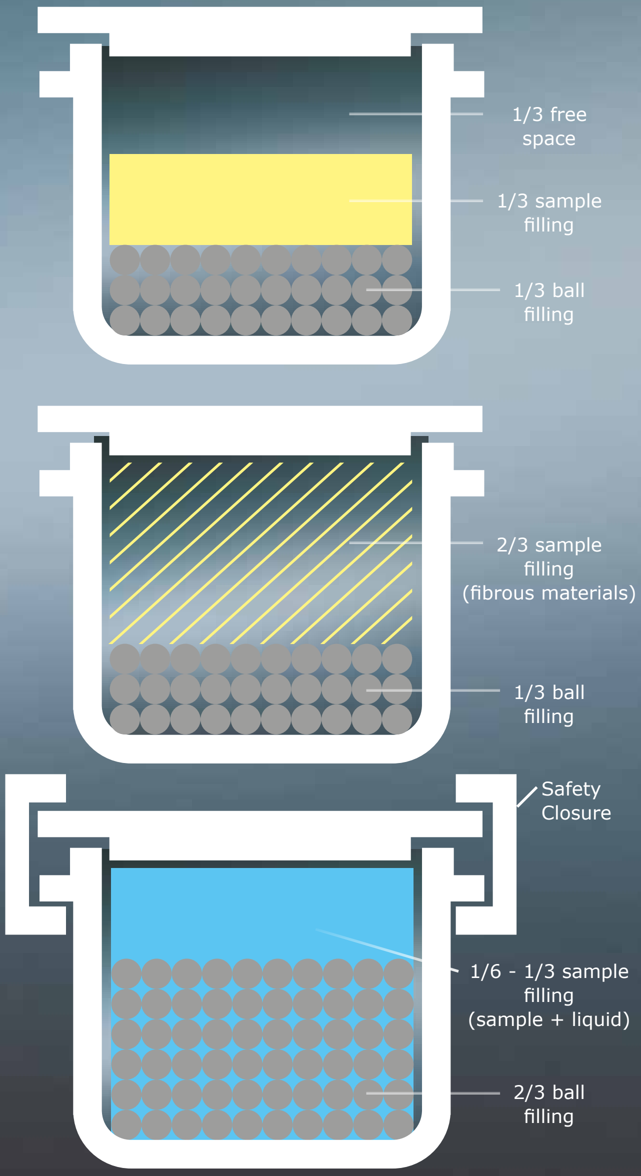
Before pulverizing a sample in a ball mill, some preliminary consideration is necessary to ensure a successful process. First, the feed size (maximum particle size) of the sample and the desired final fineness have to be established. This determines the selected grinding procedure; whether grinding needs to be done in dry or wet mode or in various steps, for example.

DRY GRINDING

This method is based on impact and friction effects and is typically used to generate **grind sizes from the low millimeter to the double-digit micron range**. For the impact effect, the grinding balls need enough space to move around in the jar. This results in a jar filling of **1/3 grinding balls, 1/3 sample and 1/3 remaining free space**. The space is needed for the ball movement as well as for possible sample expansion.

Special case: Dry grinding of fibrous materials

Fibrous sample materials tend to reduce their volume during grinding. Therefore, **the jar filled with 1/3 balls should be topped up to 100% with sample**. It may be necessary to add more sample material during grinding to maintain 1/3 of the jar covered with sample.

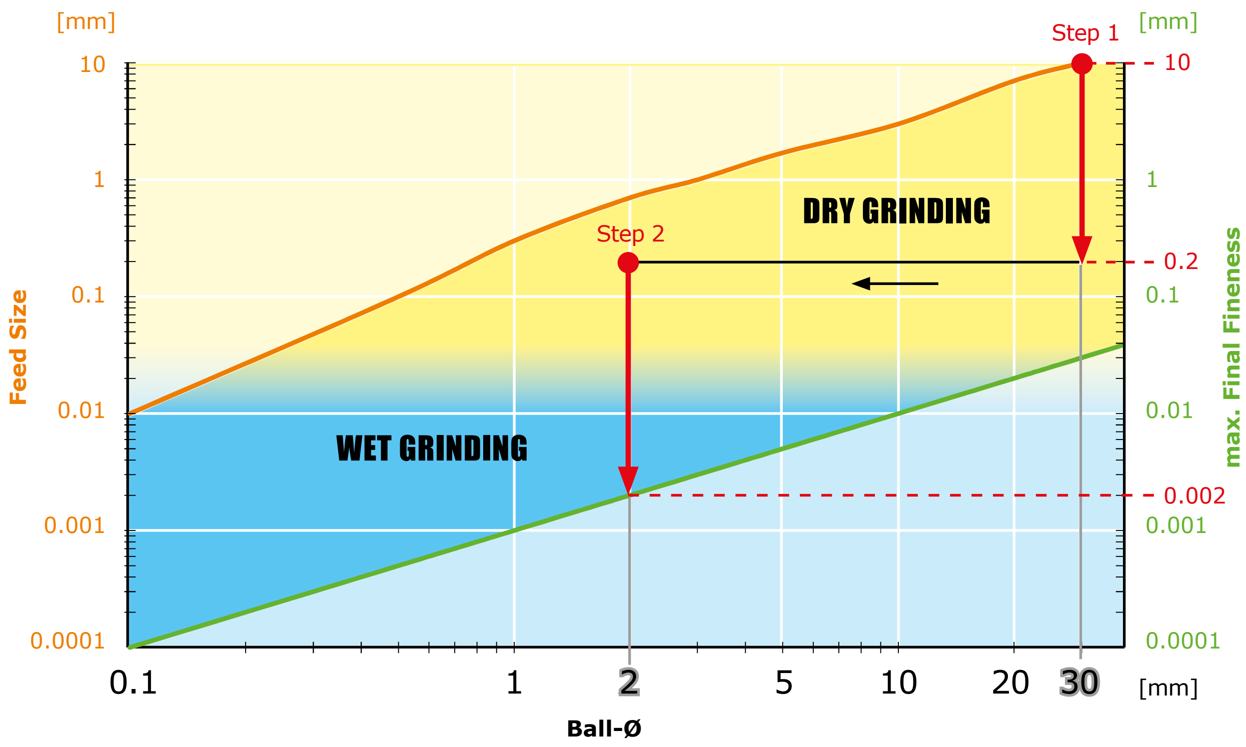


WET GRINDING

Wet grinding is carried out with high energy input and usually produces very small particles mainly based on friction. For this method, **60% of the grinding jar is filled with balls** because a larger grinding surface enables faster size reduction. Moreover, the balls do not require space to fly freely inside the jar. These high energy milling processes usually take several hours and are preferably carried out with ceramic grinding tools, for example ZrO_2 or Si_3N_4, as these are more wear-resistant than other materials.

The sample volume varies between 1/6 and 1/3 of the jar, depending on its expansion properties. Finally, liquid is added to a degree that results in a viscosity like motor oil of the whole mixture. It might be necessary to add more liquid during grinding to maintain the viscosity.

The dispersion liquid is selected according to the sample's physical properties. Generally, materials with polar properties, like minerals, are milled in water, ethanol or isopropanol whereas nonpolar samples (organic compounds) are pulverized using nonpolar solvents like petroleum ether or heptane.



CHOOSING THE CORRECT BALL SIZE

In this example, a sample with initial particle size of 10 mm is to be pulverized. According to the **rule that the selected ball size needs to be 3 times larger than the biggest particle**, a 30 mm ball is used. With balls of this size a fineness of approx. 30 µm may be achieved. Depending on the sample properties, either dry or wet grinding may be the most suitable method. If a higher fineness than 30 µm is aimed at, like 2 µm in this example, grinding needs to be done in two steps. First, the sample is milled in dry mode to a fineness of 200 µm with a Ø 30 mm grinding ball. For the next step, this is replaced by Ø 2 mm grinding balls. Due to the required fineness of 2 µm the sample is now pulverized in wet mode with 2 mm balls.

Visit **www.retsch.com/ball-charge** for the complete overview of RETSCH ball mills and recommended ball charges.

MORE TIPS & TRICKS

CORRELATION OF ENERGY INPUT AND DENSITY

The energy input of a grinding ball depends on its density. Very dense materials like tungsten carbide (WC) release a lot more energy than lighter materials like PTFE.

SELECTION OF GRINDING BALLS AND JARS

To minimize wear and abrasion, always use identical material for jar and grinding balls and do not mix different ball sizes.

THE "ALL-ROUNDER" FOR SMALL QUANTITIES

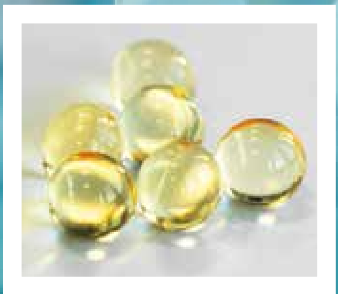
MIXER MILL MM 400

- DRY GRINDING
- WET GRINDING
- CRYOGENIC GRINDING
- BEAD BEATING
- MIXING

No matter whether ore, bone or tissue samples, hair, plants, wood, soil, plastic, minerals, pharmaceuticals or chemicals – the mixer mill MM 400, and the basic model MM 200, are proven "all-rounders" for grinding, mixing and homogenizing small sample volumes up to 2 x 20 ml. The MM 400 pulverizes hard-brittle samples like stones within a few minutes, usually to grind sizes of 100 µm or less. Typically, one large grinding ball is used for quick pulverization (high-impact mode). Tough materials like plastic must be embrittled indirectly in liquid nitrogen to improve the breaking properties prior to pulverization. The sample and the grinding ball are enclosed tightly in the jars before the jar is immersed in liquid nitrogen. As soon as the liquid stops boiling, the sample inside the jar is indirectly frozen and can be easily homogenized. Cryogenic applications may only be carried out in grinding tools made of steel. Finally, the MM 400 is also suited for grinding fibrous samples like plants or hair, usually with the help of some smaller grinding balls to increase friction. The functional principles of the MM 200, MM 400 and MM 500 are identical.

APPLICATION EXAMPLES MM 400

Sample	Grinding jar size	Grinding ball size	Material	Sample amount	Grinding time	Final fineness
Soil	35 ml	10 x 10 mm	zirconium oxide	10 g	7 min	< 20 µm
Wood	50 ml	4 x 15 mm	stainless steel	4 g	4 min	< 200 µm
Tablet, liquid filling	50 ml	1 x 25 mm	stainless steel; CryoKit	5 pcs.	1 min	< 300 µm
Chrome oxide	25 ml	1 x 15 mm	tungsten carbide	15 g	4 min	< 80 µm
Cement	35 ml	1 x 20 mm	zirconium oxide	15 g	30 s	< 500 µm
Glass	25 ml	4 x 12 mm	tungsten carbide	10 g	4 min	< 50 µm
Epoxide extrudate	50 ml	1 x 25 mm	stainless steel; CryoKit	5 g	12 min	< 200 µm
Tooth	25 ml	1 x 15 mm	zirconium oxide	1 pc.	3 min	< 100 µm
Hair	25 ml	6 x 10 mm	stainless steel	1 g	3 min	< 100 µm



CAPSULES WITH LIQUID FILLING (CRYO GRINDING)

FINAL FINENESS < 300 µM

HAIR

FINAL FINENESS < 100 µM

GREAT VERSATILITY THANKS TO EXTENSIVE ACCESSORIES

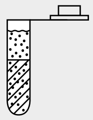
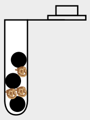
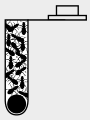
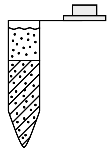
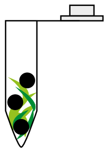
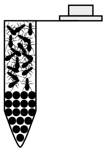
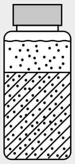
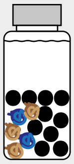
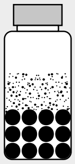
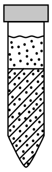
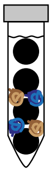
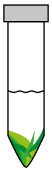
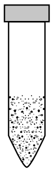
Various grinding jar sizes and materials make the mixer mills highly versatile instruments. Jars made of stainless steel are available from 1.5 to 50 ml, so the grinding jar volume can be adapted to the sample amount for efficient grinding (see pages 12-13). When neutral-to-analysis sample preparation is important, materials such as tungsten carbide, zirconium oxide or agate are used. To ensure an efficient milling process, the material of the grinding tool must be harder than the sample (see table below). A range of adapters accommodating tubes and bottles from 1.5 to 50 ml is used for biotech applications and mixing (see table on the right). With the help of the CryoKit, the MM 400 may also be used for cryogenic grinding with liquid nitrogen.

GRINDING TOOL MATERIALS FOR MM 400

Material	Density	Hardness	Abrasion resistance	Application
Hardened / stainless steel	7.6–7.7 g/cm³	≤ 245–250 HB	medium	Pulverizing medium-hard to hard and brittle samples.
Tungsten carbide	14.8 g/cm³	93.6 HRA	high	Grinding very hard, brittle sample materials.
Agate	2.65 g/cm³	6.5–7 Mohs	low	Pulverizing soft to medium-hard or fibrous samples. Agate is a high purety natural material, due to its low density it is suitable for gentle grinding with low energy input.
Zirconium oxide	6.05 g/cm³	1250 HV	high	Pulverizing medium-hard to hard and fibrous samples. It is used for heavy-metal-free grinding processes, for ultrafine milling and to prevent discoloration of the sample.

SOLUTIONS FOR BIOTECH APPLICATIONS

VIALS, BOTTLES AND TUBES AVAILABLE FOR MM 400

	Cell disruption for DNA/RNA/ proteins/ metabolites	**Cryogenic grinding of soft sample** (tissue, plants, cell pellets, insects)	**Dry or wet grinding of soft samples** (tissue, insects)	**Dry grinding of hard samples** (quartz sand)	**Extraction of pesticides from food/plants** (QuEChERS)	**Mixing of powder and wax to press pellets for RFA**
1.5 or 2 ml single-use vials **max. 2 x 10 vials**						
5 ml single-use vials **max. 2 x 5 vials**						
30 ml disposable wide mouth bottles **max. 2 x 4 bottles**						
50 ml disposable conical centrifugation tubes **max. 2 x 4 tubes**						

CELL DISRUPTION OF YEASTS, MICROALGAE AND BACTERIA ("BEAD BEATING")

Cell disruption via shearing effects, caused by small glass or ceramic beads, is a standard procedure in biological research to get access to DNA, RNA, proteins or metabolites. The beads and the cell suspension are thoroughly mixed by shaking, for example in the Mixer Mill MM 400. For the isolation of DNA or RNA less than 1 ml of cell material is needed, hence 1.5 ml or 2 ml vials are suitable. Extraction of proteins or metabolites requires larger amounts of cell suspension and can be done, e.g., in 50 ml disposable tubes. Depending on the cell types, the filling level with beads (50–80 %) and cell suspension varies just like the required time (30 seconds to several minutes).

CRYOGENIC GRINDING OF TISSUES, CELL PELLETS, PLANT MATERIALS, INSECTS

Materials like fibrous plants, tough fingernails, or tissue, are pulverized most effectively by cryogenic grinding with liquid nitrogen. Unlike the above "Bead Beating" process, the method of freezing the samples before crushing is also suitable for cracking intracellular organelles, for example of yeast. Another advantage of cryogenic grinding is the very low temperature, preventing the degradation of e. g. proteins. As soon as the cells are immersed into liquid nitrogen, cellular activities are stopped immediately and side reactions which, occur during the grinding process and alter the RNA levels, for example, are reduced.

GRINDING OF SOFT SAMPLES (TISSUES, INSECTS) OR HARD SAMPLES (QUARTZ SAND)

Homogenization of fresh tissue or insect samples is done effectively in e.g. buffer solution. It is important to use grinding balls large enough to smash the samples (5–20 mm) and to fill the single-use tubes with liquid (buffer) to get optimum mixing effects. In the 50 ml conical centrifugation tubes, 4 x 20 mm balls must be used as the tubes may break with other ball sizes or amounts. If the samples are dried, grinding is done most efficiently with grinding balls 5–10 mm, without adding any liquid (not in the 50 ml tubes). Materials like dried insects lose their volume drastically while grinding, therefore the vials may be filled to the top with sample material. In the 30 ml wide-mouth bottles, the maximum suitable grinding ball size is 10 mm. Harder samples like quartz sand are pulverized to 100 µm particles after 2 min.

MIXING OF SAMPLES OR EXTRACTION OF PESTICIDES FROM FOOD/FEED

The 50 ml tubes are very good for mixing powders or suspensions. To produce stable sample pellets with pellet presses for RFA analysis, the pulverized sample is mixed with wax (e.g. 8 g sample and 2 g wax), filled in the tubes and shaken for 1 min at 30 Hz. Another application is the QuEChERS method of pesticide extraction from homogenized food or feed samples. First, a salt mixture is produced in the tubes followed by the extraction of pesticides: 10 ml acetonitrile, salt mixture and 10 g sample; shaken 1–3 min at 30 Hz.

THE CLASSIC PULVERIZATION TOOLS

PLANETARY BALL MILLS

Planetary Ball Mills meet and exceed all requirements for fast and reproducible grinding to analytical fineness. They are used for the most demanding tasks in the laboratory, from routine sample processing to colloidal grinding and advanced materials development. They pulverize and mix soft, medium-hard to extremely hard, brittle and fibrous materials and easily achieve grind sizes down to the lower micron range. With wet grinding, particle sizes in the nanometer range can be obtained through grinding processes that run for several hours. In addition to classic grinding tasks, these mills have the necessary energy input for mechanical alloying. The strong advantage of the planetary ball mills is the option to process up to 4 x 220 ml sample in one go. Different models offer perfect adaption to all requirements – from gentle grinding of temperature sensitive samples to very high energy input for mechanochemical applications.

- DRY GRINDING
- WET GRINDING
- NANO GRINDING
- MECHANOCHEMISTRY
- MIXING

Fig. 1: The PM 100 and PM 200 are benchtop models with one or two grinding stations. The PM 400 is a floor model with two or four grinding stations which permits grinding of up to eight samples simultaneously by stacking the grinding jars.

THE "PLANETARY PRINCIPLE"

In the planetary ball mill, every grinding jar represents a "planet". This planet is located on a circular platform, the so-called sun wheel. When the sun wheel turns, every grinding jar rotates around its own axis, in the opposite direction of the sun wheel. Thus, centrifugal and Coriolis forces are activated, leading to a rapid acceleration of the grinding balls inside the jar. The resulting high pulverization energy is a prerequisite to produce very fine particles.

Example: Nano grinding of barium titanate

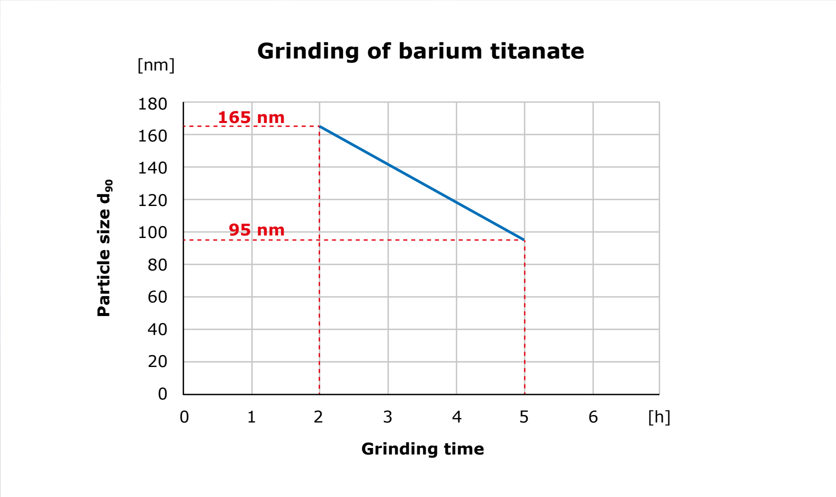


Fig. 2: Result of grinding 110 g barium titanate at 500 min^{-1} in the PM 100. After 2 hours of size reduction in 260 ml heptane with 0.5 mm grinding balls, the d_{90} value of the particle size distribution is 165 nm. By extending the grinding time to 5 h, the d_{90} value is reduced to 95 nm.

Mechanical Alloying

Another typical application with long grinding times is mechanical alloying. Here, large balls are used to produce as much energy input as possible. The PM 400 MA model is specifically designed for mechanical alloying processes with the option to process larger sample quantities. For example: 4 x 270 g Ni powder are fused with 30 g ceramic powder each in 90 min at 400 min^{-1}, using the 500 ml stainless steel grinding jars with 400 stainless steel grinding balls Ø 10 mm per jar (sample to ball ratio 1:5).

EXTENSIVE RANGE OF ACCESSORIES

The "comfort" range of grinding jars has been specially designed for extreme working conditions such as long-term trials, wet grinding, high mechanical loads, maximum speeds as well as for mechanical alloying. A wide range of materials and sizes (12 ml–500 ml) allows a largely neutral-to-analysis preparation adapted to application requirements. Due to an o-ring seal, all grinding jars are gas-tight and dust-proof. For colloidal grinding, the use of a grinding jar with a special closure device is recommended. This permits gas-tight handling inside and outside of the glove box and ensures safe transport of the grinding jar. For grindings under inert conditions, aeration covers are available. These allow for the introduction of gases like argon or nitrogen into the grinding jar. The optional GrindControl system provides full information about temperature and pressure inside the jars.

APPLICATION EXAMPLES PLANETARY BALL MILLS

Sample	Model	Grinding jar size	Grinding ball size	Material	Amount per jar	Grinding time	Final fineness
Sewage sludge	PM 100	125 ml	7x20 mm	stainless steel	25 g	10 min	< 400 µm
Dried grass	PM 100	500 ml	25x20 mm	agate	50 g	60 min	< 100 µm
Lapis lazuli	PM 200	50 ml	20x10 mm	zirconium oxide	20 g	2 min	< 90 µm
Silicon carbide	PM 400	500 ml	60x15 mm	zirconium oxide	400 g	20 min	< 70 µm
Activated coal	PM 100 CM	250 ml	15x20 mm	stainless steel	40 g	15 min	< 45 µm

FASTER – FINER – COOLER

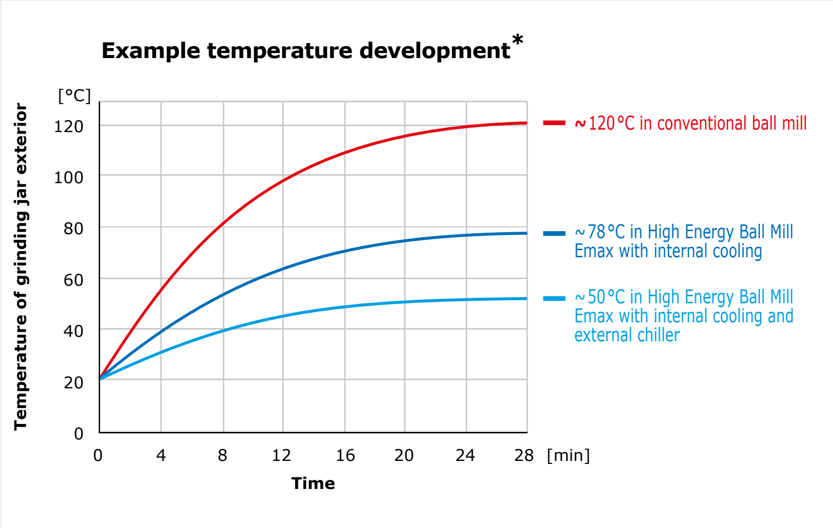
HIGH-ENERGY BALL MILL Emax

- DRY GRINDING
- WET GRINDING
- NANO GRINDING
- MECHANOCHEMISTRY
- MIXING

Among the versatile range of RETSCH ball mills, the High Energy Ball Mill Emax stands out as the perfect solution for producing nanosized particles in a fraction of the time a conventional ball mill needs. The Emax is unique in many ways: the maximum speed of 2000 min^{-1}, the special jar geometry and the innovative liquid cooling system all make this mill the most effective and powerful size reduction tool, especially for research applications.

HIGHLY EFFICIENT COOLING SYSTEM MAKES COOLING BREAKS OBSOLETE

The greatest challenge of a high energy ball mill is keeping the temperature under control as the enormous size reduction energy leads to considerable heat built-up inside the grinding jar. This was solved in the Emax by integrating an innovative water-cooling system which cools the grinding jars via the jar brackets. This is much more effective than, for example, a fan system, as heat is more easily discharged into water than into air. Hence, the Emax usually does not require cooling breaks which are typical for long-term processes in conventional ball mills even at low speed. In addition to the internal cooling, the mill can be connected to a chiller or the tap to further reduce the temperature.



*Temperatures depend on sample material, instrument configuration, and ambient temperature and may differ from this example.

Fig. 1: The effect of the integrated cooling system of the Emax can be further increased by connecting the mill to an external chiller.

CONSIDERABLE TIME SAVINGS

The high energy input is a prerequisite for producing nanosized particles or new materials in mechanochemical processes. The maximum speed of 2000 min^{-1} in combination with uninterrupted grinding processes lead to considerable time savings compared to all other ball mills.

The following example from the field of pharmaceutical research shows how the Emax opens up new possibilities for size reduction of thermally unstable ingredients.

A cortisone derivative was pulverized in the Emax for 5 min to below 300 nm without exceeding the critical temperature limit of 45 °C. The conventional ball mill required a net grinding time of 30 min with an additional 2.5 hours for cooling breaks.

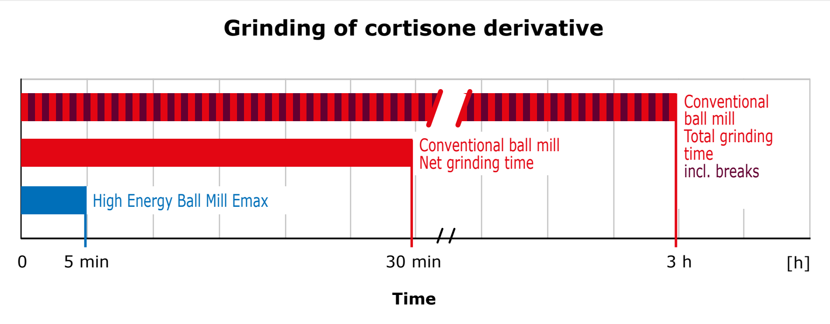


Fig. 2: The time saving with the Emax compared to a conventional ball mill when grinding cortisone derivative is almost 3 hours.

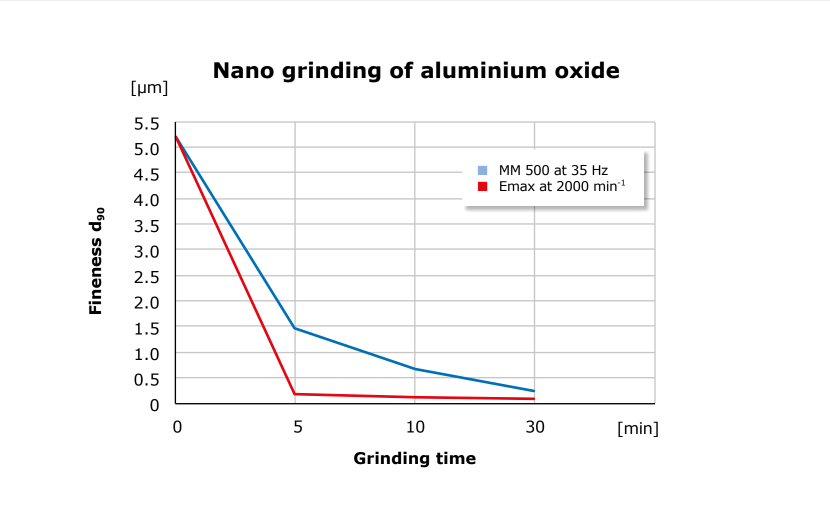


Fig. 3: Nano grinding of aluminum oxide in the Mixer Mill MM 500 and the Emax.

Another example for the very efficient grinding principle of the Emax is grinding of aluminum oxide. The same sample was ground in the MM 500 which also allows for continuous grinding without cooling breaks. Due to the high energy input at 2000 min^{-1}, which is only possible with effective water cooling, the Emax delivers particle sizes of 0.18 µm after only 5 min processing time.

Internal liquid cooling system

TEMPERATURE UNDER CONTROL

The Emax software allows the user to carry out the grinding process within a defined temperature range with a minimum and maximum temperature. On reaching the maximum temperature, the mill automatically interrupts the grinding process and resumes it when the jar has cooled down to the minimum temperature. The possibility to define a maximum temperature is essential for grinding heat-sensitive sample materials.

Polysaccharide is a good example to demonstrate the positive effect of the automatic temperature control on grinding temperature-sensitive samples. Here, the maximum allowed temperature during grinding is 80 °C. When using conventional ball mills, the appropriate cycles of grinding and cooling need to be ascertained by empirical trials which may either lead to degeneration of the sample or to extended processing times. The Emax, in contrast, allows for variable cycles of grinding and cooling within the defined limits of the temperature control mode. Thus, the entire size reduction process remains reproducible and is carried out in the shortest possible time.

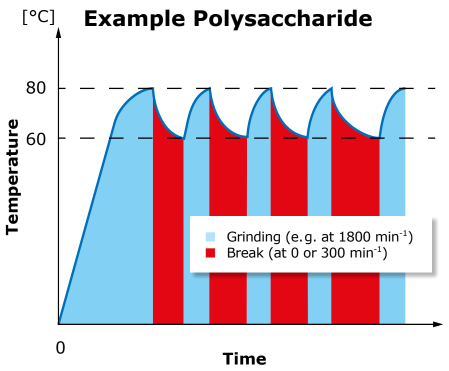


Fig. 4: Grinding of polysaccharide in a defined temperature range between 60 °C and 80 °C. Break times were automatically adjusted by the Emax software.

PRESERVING CRYSTALLINE STRUCTURE
XRD-MILL MCCRONE

James Utley, Research Assistant at the Earth Science Department at Liverpool University, explains why the XRD-Mill McCrone is the perfect choice for sample preparation prior to XRD analysis.

The analytical technique of XRD was discovered more than 100 years ago and helps to answer interesting questions like: Can clay minerals tell us about Earth's past climate or how do minerals present in fault zones affect earthquakes?

X-Ray Diffraction measures the structure of crystalline materials; some minerals are stronger, and more resistant to changes in temperature than others. To represent a crystal structure, think of a child's climbing frame, the distance between the bars being the identifying features. If you drive a bulldozer into the climbing frame you will bend it, changing its structure, and making it rather hard to identify!
So, we need to:

- **PRODUCE A VERY FINE, WELL MIXED POWDER WITH A NARROW RANGE OF PARTICLE SIZES**
- **AVOID HIGH IMPACT FORCES AND HIGH TEMPERATURES**

This is where the XRD-Mill McCrone enters the lab as the only milling machine capable of fulfilling all criteria for reliable sample preparation to X-Ray Diffraction.

The grinding set comprises 48 aligned cylinders, each approximately 12x12mm. The material of the grinding set can be chosen to suit the application: zirconium oxide, corundum, or agate. Numerous small grinding elements provide many more contact points than, for example, equivalent sized ball mills. These elements slide past each other, as well as bumping into each other during the circular oscillation of the instrument. Repetition of grinding 'contacts' takes precedence over the energy of each impact.

A grinding/lubricating fluid must be added to the sample, typically distilled water, but alcohol can be used when water-soluble minerals are suspected. The addition of a grinding fluid produces an even more effective grinding slurry, ensuring all particles are circulated through the mill, and keeps the sample fragments cool.

In summary, the XRD-Mill McCrone fulfills all criteria for X-Ray Diffraction of minerals as it produces a fine powder with a narrow particle size distribution and preserves the crystalline structure of the sample by avoiding high impact forces and high temperatures.

FOR LARGE VOLUMES
DRUM MILL TM 300

While ball mills come in a variety of shapes and sizes, the maximum sample volume to be processed is comparatively small and does not exceed 880 ml. With RETSCH's TM 300 Drum Mill, however, it is possible to prepare up to 20 liters of sample material in one go.

This drum mill can be operated either as a ball mill or as a rod mill by using the corresponding module. The standard sizes of the grinding drums range from 5 to 43.4 l. The TM 300 is suitable for dry or for wet grinding, and achieves a final fineness down to 20 µm, depending on the sample material.

In a drum mill, the usually pre-crushed sample is placed inside the drum with the grinding media, i.e. balls or rods, and is subjected to external forces. As the drum mill has a variable but low speed of 15 – 80 min^{-1}, it is the only ball mill where mixtures of ball sizes are allowed. This can be beneficial to reduce grinding times.

The TM 300 features a yoke and locking mechanism for easy access to the sample. In the standard 21.5 l drum, a 20 kg ball filling, Ø 20 mm, is used. Ball sizes 5 mm, 10 m or 30 mm are also common. A sufficient number of balls or rods is required for an effective grinding process.

The drum cover is easily removed for cleaning thanks to a quick release locking mechanism. The mill is equipped with a solid noise-protection hood.

EXAMPLE: GRINDING OF MUSHROOMS

140 g dried mushrooms were ground to 100 µm in 90 min at 60 min^{-1}, in a 10 l drum with 10 kg of 20 mm stainless steel grinding balls.

APPLICATION EXAMPLES DRUM MILL TM 300

Sample	Drum size	Grinding ball size	Material	Sample amount	Grinding time	Final fineness
Titanium slag	21.5 l	20 mm (20 kg) + 10 mm (13 kg)	stainless steel	4.4 l	12 h	< 30 µm
Cellulose fibers	21.5 l	30 mm (20 kg) + 40 mm (11 kg)	stainless steel	12 l	15 h	< 50 µm