ATTRITOR MILL: Standard operating procedure

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Description

The mill operates by moving milling tools inside the milling vial; the milling tools are agitated by a spinning impeller. The adjustable parameters are the operating speed (rpm), cooling type, and installed lid type. The milling vial currently in the set up is the 750cc stainless steel which has the suggested factory loading of 200 g of powder material and 1.814 kg (4 lbs) of steel balls. The cooling can be by room temperature water or liquid nitrogen (LN). Alternatively, the cooling jacked can be evacuated to reduce the heat transfer rate to the surrounding air.

Before starting:

1) Ensure that the work area is clear of dust, debris, material samples, and any lab components not directly used for the experiment. Use cleaning solution to prepare the countertop surface prior to start.
2) Determine the type of milling experiment desired. Identify milling parameters for your specific experiment. Select among the following milling parameter options:
    a. *Use of Process Control Agent (PCA)*: PCA inhibits formation of agglomerates and/or cold-welding. Some PCAs used are stearic acid and hexane.
    b. *Wet or Dry Milling:* "Wet" milling requires the use of liquid process control agent during the milling.
    c. *Vial Atmosphere:* Inert atmosphere requires loading vials inside the glove box which contains argon. See glove box instructions for details. For standard vials, alternatively, inert gas can be filled using customized vial lids equipped with valves.
    d. *Milling media*: Varied ball sizes are available for use as well as other milling media.
    e. *Charge ratio*: Mass ratio of the milling media to the powder sample
    f. *Milling time*: Needs to be determined before the experiment
3) Locate the necessary tools for opening, closing, loading, and mounting milling the milling vial. Clean the tools before use.
4) Locate materials to be used as starting components
5) If the experiment involves introducing LN into the milling vial, prepare a Dewar filled with LN prior to connecting the cooling ports of the cooling jacket.
6) Determine the type of cooling to be used
    a. For water cooling, connect the water lines (plastic tubing) from the fume hood to the respective inlet/outlet ports of the cooling jacket.
    b. For liquid nitrogen cooling, connect the copper tubing to the outlet port of the cooling jacket and the liquid nitrogen feed from the tank to the inlet port of the cooling jacket.
    c. For use of vacuum, attach vacuum line to any cooling jacket port and plug the other port.
7) Determine which vial lid will be used; following are the lid types available:
    a. Inert Gas Lid – Allows the feed of a gas through lid. Requires the milling assembly to be completely sealed to work properly. Gas flow can be regulated with the flow meter. A bubbler is attached to the lid outlet port to indicate gas flow. The assembly with this lid is rated for a 10 psig. It can be used in combination with the external LN cooling.

b. Cryogenic Lid – Allows the feed of liquid nitrogen inside the milling vial without having to stop the run. A funnel is attached to the inlet port to facilitate the introduction of LN. Material leak may occur if the lid is not properly sealed.

Loading milling vial:

1) Place the vial inside a fume hood.
2) Weigh the milling balls and the powders in separate weighing cups, one cup for each type of powder, and transfer them into the vial.
   Note: when loading powders, ensure no cross-contamination between samples and stock material.
3) For wet milling measure the necessary amount of process control agent in a separate jar.
4) Inside the fume hood, pour the process control agent into the vial.
5) Important: **double check that the jar that contained PCA is empty** which means that PCA was poured into the vial. It is important to ensure that materials requiring wet milling are not milled without PCA.
8) Place the milling vial inside the cooling jacket. Place the gasket between the milling vial and the metal spout before securing the holding nuts. Afterwards, properly attach the lid and lid gasket on top of the milling assembly.

During the milling run:

1) Establish an appropriate cooling operation:
   a. Using LN inside the vial: first cool the vial externally. Do not fill in LN inside the vial before it is thoroughly cooled to minimize LN boiling and removal of the powder from the vial. Fill in LN while monitoring its level using the view hole (which can be opened removing the bolt blocking it for routine operation) and a flashlight. The LN level can be monitored before or during the milling. Refill LN as needed, suggested refill rate is 3 times per hour.
   b. Using LN for external cooling: Adjust the valve to achieve a continuous LN flow. Alternatively, the cooling jacket can be filled and refilled periodically. Suggested refill rate is 3 times per hour. Periodic inspections of the LN cooling are needed, at least every 20 min.
   c. Using water cooling (external): use the cold water (CW) valve in the fume hood to establish a continuous water flow.
2) Monitor milling operation at least once every hour
3) It is possible to set up "after hour" runs for preparing samples using an established protocol. Such runs cannot be setup if LN cooling is used.
4) NOTE: Material can leak out if the cryogenic lid is used or if the assembly is not sealed properly. Periodically clean the work area using hexane soaked paper towels. **Do not use dry paper towels.**

Extraction of the prepared samples:

NOTE: The material prepared may be reactive in air, it is important that the protocol is followed. Make sure to wear goggles, lab coat, and cryogenic gloves (if working with LN cooled setup).

1) After completion of the ball-milling run, allow the mill to dry for 12 hrs before starting the recovery unless wet milling or cooling inside the milling vial is used. All sample

collection must be conducted inside the glove box filled with inert gas.

2) When inert gas lid is used, allow the feed of gaseous nitrogen trough the vial for 10 min after the milling is completed.
3) When using LN inside the vial: remove the vial and place it immediately in the airlock of the glove box. Turn on the vacuum pump and allow the vial to warm up to room temperature within the airlock.
4) When using LN or water for external cooling: allow the milling media to dry for 12 hrs before starting the powder recovery. After making sure the milling media is completely dry, take out the milling vial and immediately place it inside the airlock of the glove box. Turn on the vacuum pump and allow the powder to passivate for 4 hrs before taking vial inside the glove box.
5) Transfer the vial inside the glove box for sample collection.
6) If a new, unknown material is formed, determine if the material is pyrophoric.
    a. Carefully remove a small powder sample with a spatula into a small recovery pan and close the sample with recovery pan lid.
    b. Place the recovery pan with the small amount of sample inside the airlock and expose it to air for at least 3 minutes to determine the material's pyrophoricity. If the material does not show any pyrophoric behavior, take the small recovery pan inside the sample burning fume hood. Using a clean spatula, place very small amounts (few milligram) of sample on a dry paper towel and close the fume hood immediately. Observe the sample for signs of smoke or sparks for 3 min.
    c. If the material is pyrophoric, leave the milling vial inside the glovebox with the lid cracked open for 24 hours. Check whether the material is passivated by repeating steps described in part 6b. After the material is passivated store all the samples inside the glovebox.
7) Remove materials from the vial by washing it out with hexane. A suction assembly (found in the fume hood) can be used to collect the solution. If vial needs to be cleaned of the sample leftovers, it is possible to use brush only for wet material. One approach is to simultaneously brush and apply the solvent using a squeeze bottle. **Do not use brush, spatula, or any other tool to remove dry powder from the vial.** Use of spatula with dry powder is only possible when
    a. the vial contains substantial amount of powder
    b. is inside the glovebox
    c. or if the powder is well known to be inert
8) Upon collection completion, transfer the material to the collection container.
9) For most materials, it is recommended to store them under hexane.
10) When preparing samples for characterization, remove only the necessary quantities in a separate storage bottle for that specific characterization test. **Do not remove the entire storage bottle from the glove box.**
11) After completely extracting the material, clean all tools used and wipe down the surfaces with solvent. Properly dispose all the waste.