CARBOLITE-GERO GMBH & CO. KG 3-ZONE FURNACE STANDARD OPERATING PROCEDURE

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Section 1: Purpose

This document specifies the standard operating procedure (SOP) for loading and unloading the 3-zone Carbolite-Gero high temperature furnace for sealed tube high temperature reactions (max 1300/1350 °C).

Section 2: Application

The 3-zone Carbolite-Gero high temperature furnace provides a large range of processing conditions for synthesizing precursors and single crystals of various materials, such as metal chalcogenides and related compounds.

Section 3: Equipment, Chemicals and Supplies

Fused quartz tubes are purchased from GM Associates, cut to desired length, and sealed on one end. After samples are loaded, tubes are sealed either by heating and twisting or by sealing a smaller capped tube inside the larger tube. Tubes may be purchased from other vendors but must be either flame-fused or electrically-fused quartz.

Mullite tubes are purchased from Anderman Ceramics and may be purchased from other vendors with 62.6% alumina content, maximum working temperature greater than 1350 °C, and low thermal expansion coefficient ($<5.8 \times 10^{-6}$ /K) between 20 – 1000 °C.

Insulating wool can be purchased from a variety of vendors and should be rated for use at appropriate heating temperature (aluminum silicate wools for temperatures above 1250 °C and calcium silicate wools for lower temperatures).

Common chemicals used include molybdenum, tungsten, sulfur, and selenium powders and their metal chalcogenides. Molybdenum or tungsten chloride/oxide/oxychloride may be present in some transport reactions (<10 mg/mL total). Chemicals are typically purchased from Sigma or Alfa Aesar in high purity (99% or higher).

Section 4: Personal Protective Equipment

Due to the hazards associated with heating contents under pressure, all possible precautions must be taken to ensure safety. The following equipment should be used:

- Safety glasses are mandatory at all times
- Chemically resistant acid-compatible lab apron or lab coat.
- Gloves:
    - For loading tubes with samples: nitrile gloves or other chemically compatible gloves
    - For handling hot samples or containers that pose the risk of rupture: thermal gloves
- Closed-toe shoes (no sandals) and pants (no shorts).
- When handling a sample that poses a risk of rupture, **WEAR A FACE SHIELD** in addition to personal protective equipment listed above.

Section 5: Operational Procedures

Note: New users must be trained by GLA in charge of furnace and complete BI-MMRC safety training before using or modifying programs and must obtain approval for use of chemicals other than those listed in Section 3. Users must also be able to modify programs and operate the regulators according to the "Short description" manuals.

Sample Preparation

1. Samples should be carefully sealed in a fused quartz ampule under vacuum (<0.1 Torr) and wiped down on the outside with isopropanol to remove sample residue and avoid contaminating the mullite tube in the furnace.
2. High-pressure rated fused quartz tubes typically can withstand 10-15 atm,; however, their rating may be lower depending on tube sealing method. Load tubes based on the approximate amount of volatile species present at annealing temperature and size of tube. Calculate that the pressure due to all volatile species at the maximum temperature is less than 5 atm.

   DO NOT exceed 0.05 mmol/mL of EXCESS volatile species per tube. Ramp extra slowly (≤1°C/min) for syntheses containing >0.5 mmol/mL volatile starting materials. Do not load more than 10 g of starting material in all tubes combined...

Note on loading limits: *Check literature for vapor pressure of volatile species at various temperatures to determine an appropriate annealing temperature at which pressure does not exceed 5-10 atm.*

Initial Checks

3. Fill out the log book, making note of the user name, the loading date, estimated run time, and contents of reaction tubes in the log book. Include comments on number of segments and dwell times at various temperatures.
4. If the controller is not on, turn it on by turning the red switch to the "ON" position (vertical).

5. Check that the center regulator does not have “RUN” showing along the top. If it is, press and hold the “RUN/HOLD” button until the lamp “RUN” disappears. Ensure the target value below the actual temperature displayed is below 40 °C (automatic set point). (Press “A/MAN” button to toggle to automatic mode in order to set target temperature).
6. Wearing the appropriate PPE, check that there is no sample inside the furnace and the mullite tube is present and clean. If necessary, clean the inside of the tube with isopropanol.

Sample Loading

7. If the furnace is reading below 40 °C, raise fume hood sash and load sample to the appropriate depth in the tube.

Note: Never load a sample directly into the furnace without the large mullite tube.

8. Place insulating wool over the ends of the large mullite tube once all samples have been loaded to make a tight plug.
9. Place blast shield over the end of the furnace which is facing work area in hood.
10. Lower fume hood sash. Attach a “Furnace In Operation” sign to the fume hood.

While furnace is in operation (“RUN” mode), keep fume hood sash closed and blast shield in front of the end facing open space.

Start-up and Running a Program

11. Wear clean gloves when operating controller regulators, buttons and switches.
12. Press the picture and parameter keys simultaneously to go to the main menu. To use a program, press “A/MAN” to toggle to the automatic setting.
13. To modify a program, press the picture key until “Program Edit” appears, select the appropriate program number, and press the parameter key to scroll through the program segments and change settings using the arrows (plus and minus keys).

Refer to “Short description 3508” for segment types and program settings for the center regulator (zone 2). Refer to “Short description 3216” for settings for side regulators (zones 1 and 3).

14. Press “RUN/HOLD” on main regulator until the lamp “RUN” appears.
15. Furnace will cool down to the automatic set point once program has ended.
16. To stop a program, press and hold the “RUN/HOLD” button until the “RUN” lamp disappears.

Sample Unloading

17. Similar to loading procedures, **when the furnace has cooled down to below 40 °C in all three zones and the regulator is not reading “RUN”**, raise hood and unload the sample.

Load and unload sample only while furnace is below 40 °C and not running (“HLD” mode or OFF), during which time fume hood sash may be raised.

18. Check that the inside of the mullite tube is still clean and wipe with isopropanol if necessary.

19. The furnace may be left on stand-by with a set temperature below 30 °C (use arrow keys to set temperature on the main menu in automatic mode), or turned off with the main red power switch.

Section 6: Primary Hazards

All sealed ampules under pressure pose a danger of exploding, especially during heating or cooling. Metal powders are fire hazards and will combust upon exposure to air at high temperature. Explosions of tubes containing volatile compounds pose immediate health hazards to any persons exposed to the released gases, which usually contain a mixture of oxides and anions which form corrosive compounds upon contact with water. Metal oxides and powders are eye, skin, nose, throat, and lung irritants. Common chemicals used include, but are not limited to, molybdenum, tungsten, sulfur, selenium powders and their metal chalcogenide products.

Sulfur oxides:

Sulfur oxides and other byproducts of sulfur combustion form intensely irritating and corrosive compounds. Exposure to sulfur dioxide gas (10-50 ppm) for 5-15 min causes burning of the eyes and respiratory tract, and forms sulfurous acid upon contact with moist membranes.

Selenium oxides:

Selenium dioxide is corrosive to the eyes, skin and respiratory tract. Toxic fumes are released during a fire.

Transport Agents:

Molybdenum and tungsten oxides, chlorides, and oxychlorides are typically used in transport reactions and are corrosive compounds which cause skin, eye, and respiratory irritation.

Section 7: Engineering Controls to Prevent and Mitigate Hazards

All operations with sealed ampules above room temperature must be performed in a fume hood, which is close to an eye wash station and shower. Mullite tubes are plugged on both ends with insulating wool to absorb some gas leakage and the blast shield protects other areas of the fume hood from possible explosion fragments and mitigates gas release.

Section 8: First-aid and Emergency Procedures

Explosion inside fume hood during furnace operation:

i. Keep fume hood sash lowered.

   If fumes and/or irritants are detected outside the hood, lower the fume hood sash and immediately evacuate all personnel from the room. Obtain first aid for inhalation and skin/eye contact. Inform a safety officer immediately.

ii. Turn off main power switch (red).

iii. Instruct others in the vicinity to keep sash low and/or post a sign with these instructions until any smoke has dissipated and furnace has cooled to below 30 °C.

iv. Once it is safe, remove any broken glass/quartz and follow appropriate waste disposal procedures.

v. For large explosions (total mass > 5 g), degas the furnace by heating to 1000 °C overnight before further use.

Inhalation of metal or chalcogen powders/oxides:

If a large amount of toxic gases are inhaled, move to fresh air immediately and rest in half-upright position. Seek medical attention.

Skin contact with metal or chalcogen powders/oxides:

Remove contaminated clothing and immediately wash affected area with cold water for 15 minutes. Seek medical attention if irritation or burns persist after washing.

Eye contact with metal or chalcogen powders/oxides:

Immediately flush eyes with running water for 15 minutes, lifting lower and upper lids occasionally, and remove contact lenses if necessary. Obtain medical attention.

For chemicals not detailed here, follow emergency procedures specific to chemicals in case of eye or skin contact with the chemical being handled. Safety data sheets are available in Noyes 221 and online at http://www.safety.caltech.edu/sds