Standard Operating Procedure (SOP): Hydrothermal bomb reactions (HT_bomb_reactions)

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Principal Investigator:	Dr. Andreas Kafizas		
Date of approval:		Date for review:	

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1. Justifying the hazards

Can the substance or process be substituted or modified with a less hazardous version? Can the volume be decreased?

Identify hazards with specific risk assessments and a College or a departmental approval process			
Ionising radiation sources	☐	Biological sources (microorganisms, human/animal tissues, plants)	☐
Class 3R, 3B or 4 Lasers	☐	Offsite work	☐
Confirm if Lone working is permitted with this SOP? ☐ If it is permitted, describe the control measures for lone workers:			

2. Training and lone working

All users should be trained by a competent user before beginning any independent work on this reactor.

THE SETUP OF HYDROTHEMAL BOMBS, OUTSIDE OF REGULAR WORKING HOURS, IS NOT ALLOWED. HOWEVER, THEY CAN BE LEFT TO RUN OVERNIGHT IF THE TEMPERATURE AND REACTION HAS BEEN DEEMED TO BE STABLE (SEE SECTION 4)

3. Overview of equipment and checks

3.1 Hydrothermal bomb

The hydrothermal bomb we have available is from Sci Med, https://www.scimed.co.uk/product/hydrothermal-synthesis/. They come with a batch Declaration of conformity from Parr, they are PED standard engineering practice vessels, and designed under the ASME code. The product has the following ratings, https://www.parrinst.com/products/sample-preparation/acid-digestion/large-capacity-acid-digestion-vessel-model-4748-125-ml/:

- Body: stainless steel body with 6 six cap screws in the screw cap to seal the flanged PTFE cup
- Liner: PTFE (Poly Tetra Fluoroethylene: Highly chemically resistant. Resistant to Acid and Alkali, and various organic solvents)
- An expandable wave spring maintains continuous pressure on the seal during the cooling cycle when PTFE parts might otherwise relax and leak.
- A safety blow-off disc above the PTFE cup will release pressure through an opening in the vessel head if pressure should accidentally reach the 3500 psi range (240 bar).
- For safe operation, pressures in these vessels should never exceed 1900 psi (130 bar) and temperatures must not exceed 250 °C.

Figure 1: Photograph of the hydrothermal bomb from Parr.

3.2. Solvent choice, and filling the bomb

The hydrothermal bomb should never be fully filled with liquid. Leaving sufficient headspace is essential to avoid potential explosions. The amount of headspace that should be retained is dependant on:

1. Solvent
2. Temperature

3.2.1. Water

FOR WATER, A MAXIMUM TEMPERATURE OF 200 °C HAS BEEN CHOSEN, WITH A MAXIMUM FILL VOLUME OF 140 ml.

Figure 2 shows the pressure-temperature phase diagram of water. The maximum pressure rating of the hydrothermal bomb is 130 bar, which corresponds to a temperature of ~325 °C, which is within above the designated limit

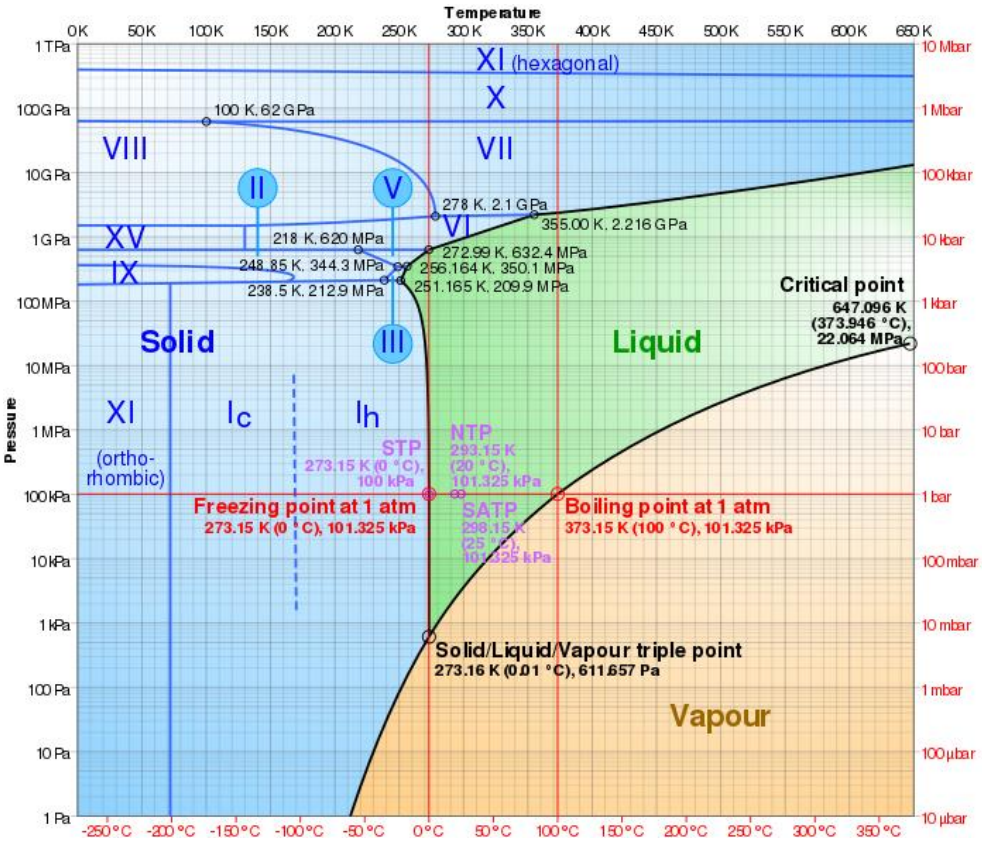

Figure 2: Pressure-temperature phase diagram of water.

Figure 3 shows the density-temperature phase diagram of water. For the maximum permissible temperature allowed for water in this bomb (200 °C, which results in a pressure of 20 bar), the density of water is ~870 kg/m^3. At room temperature the density of ethanol is ~997 kg/m^3. This means that at 200 °C, the volume of water has expanded by a factor of ~1.2. As the total volume of the vessel is 200 ml, this means that a headspace of at least 40 ml should be maintained to avoid over-stressing the bomb.

NOTE: If the bomb is over-filled, due to the volume increase generated by the temperature increase, an enormous hydrostatic pressure is generated. The loading limits we prescribe for these bombs are conservative to ensure that the energy released from the sample will not overstress the bomb.

In order to avoid over-stressing the bomb, a maximum permitted fill volume of 140 ml of water is allowed.

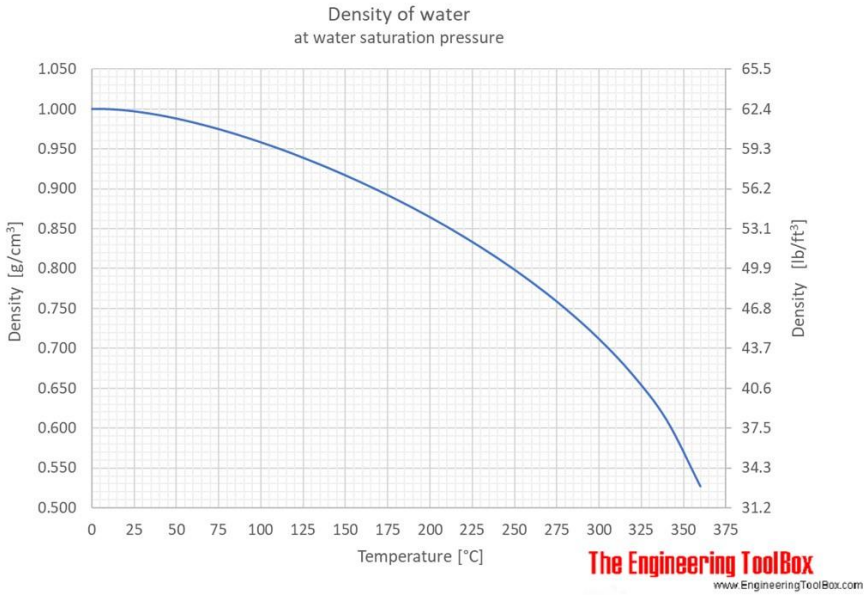

Figure 3: Density-temperature diagram of water.

3.2.2. Ethanol

FOR ETHANOL, A MAXIMUM TEMPERATURE OF 200 °C HAS BEEN CHOSEN, WITH A MAXIMUM FILL VOLUME OF 100 ml.

Figure 4 shows the pressure-temperature phase diagram of ethanol. The maximum pressure rating of the hydrothermal bomb is 130 bar, which is within above the designated limit

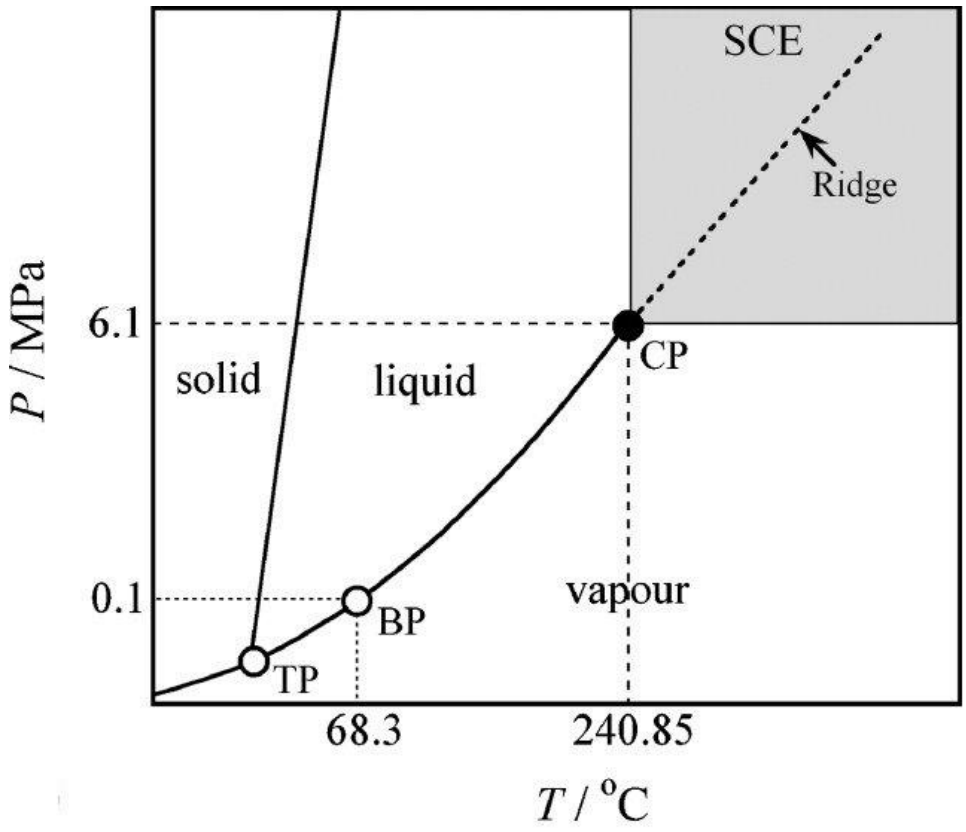

Figure 4: Pressure-temperature phase diagram of ethanol.

Figure 5 shows the density-temperature phase diagram of ethanol. For the maximum permissible temperature allowed for ethanol in this bomb (200 °C, which results in a pressure of ~30 bar), the density of ethanol is ~550 kg/m^3. At room temperature the density of ethanol is ~780 kg/m^3. This means that at 200 °C, the volume of ethanol has expanded by a factor of ~1.4. As the total volume of the vessel is 200 ml, this means that a headspace of at least 60 ml should be maintained to avoid over-stressing the bomb.

NOTE: If the bomb is over-filled, due to the volume increase generated by the temperature increase, an enormous hydrostatic pressure is generated. The loading limits we prescribe for these bombs are conservative to ensure that the energy released from the sample will not overstress the bomb.

In order to avoid over-stressing the bomb, a maximum permitted fill volume of 100 ml of ethanol is allowed.

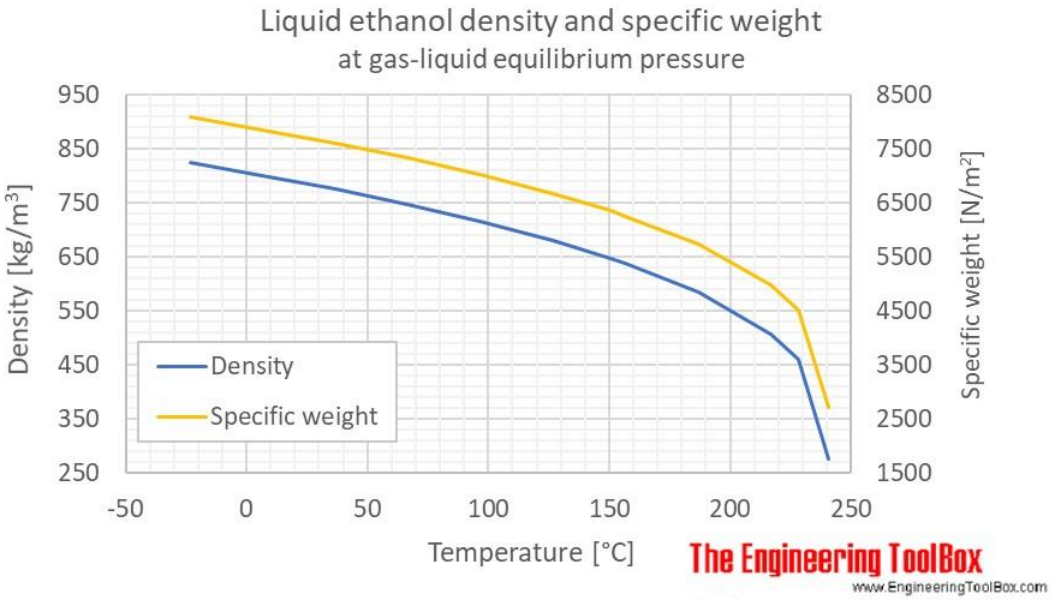

Figure 5: Density-temperature diagram of ethanol.

4. Setting up the oven

All hydrothermal reactions should be carried out in the closed oven located in B01 (never on a hot-plate and never in the furnace). This is because the oven in B01 cannot surpass 240 °C, meaning that the autoclave is unlikely to explode. All users must be trained on how to use the oven by a competent user before using the oven. When booking the oven the user should state their name, temperature they will use and general reaction information (e.g. Andreas, 200 °C, hydrothermal synthesis of TiO2 in water).

To ensure the reaction does not exceed the prescribed heating limits, the maximum permissible temperature on the oven should be set to:

- 200 °C for reactions in water (and a maximum fill volume of 140 ml)

- 180 °C for reactions in ethanol (and a maximum fill volume of 120 ml)

The heating and cooling rates should be set to a maximum of 5 °C/ min.

All reactions should begin and end at room temperature.

Adequate signage should be placed on the oven to warn others that a hydrothermal reaction is taking place, and not to disturb this reaction (*i.e.* the oven should not be opened, the settings on the oven should not be changed *etc*).

Once a reaction is started, the user should check that the oven reaches the desired temperature, and does not exceed this temperature (or the maximum permissible temperature). If, for some reason, the maximum temperature is exceeded, the oven should be turned off immediately, and the reaction allowed to cool to room temperature before handling.

5. Procedure

Prepare the metal salt solution, in a given solvent (NOTE: refer to section 3.2 for the total allowed fill volume and temperature). All mixing should be carried out in a fume hood to minimise spill risk. Refer to the COSHH for the given reaction for any additional associated risks.

FOR REACTIONS IN WATER, A MAXIMUM TEMPERATURE OF 200 °C IS ALLOWED, WITH A MAXIMUM FILL VOLUME OF 140 ml.

FOR REACTIONS IN ETHANOL, A MAXIMUM TEMPERATURE OF 200 °C IS ALLOWED, WITH A MAXIMUM FILL VOLUME OF 100 ml.

Add the salt solution to the Teflon liner. Ensure that sufficient head space remains to avoid over-stressing the bomb when heated. Close the lid on the Teflon liner and place with the steel bomb. Tighten the 6 screws on the main body of the steel bomb touch tight. DO NOT CLOSE THE LID TOO TIGHTLY. Place the bomb within the oven and ensure that the oven has the correct settings (see section 4 for more details). Ensure that adequate signage is placed on the oven to warn others that a hydrothermal reaction is taking place. Once the reaction is complete, and the bomb has reached room temperature, the bomb can be open using the steel bar if needed (NOTE: if the bomb becomes hard to open, grease the thread using the WD40 oil or carbon based lubricant available in B01). Open the Teflon lining and filter the product. This can be done by gravity (if the particles are sufficiently large) using filter paper and a funnel, or under suction using a sintered glass funnel. The product should be washed (typically using the solvent it was made in), and then dried in a ceramic boat (typically oven dried).

6. Disposal of spent solvents

Spent solvents should be disposed of appropriately. Non-chlorinated solvents should go in the non-chlorinated solvent waste bin. Chlorinated solvents should go in the chlorinated solvent waste bin. Spent solutions should never be washed down the sink.

7. Personal Protective Equipment (PPE)

Given its location in a working laboratory, the user is required to wear safety specs and a lab jacket at all times when using this apparatus.

8. Risk Analysis of SOP and emergency procedures

(In addition to Dept. Safe Lab Practice)

Always remember to include fire associated risks and control measures where appropriate

Hazard	Raw risks	Current control measures	Residual risk (Low/Med/High)
Bomb	Explosive capability	**ALL WORK MUST BE CARRIED OUT IN A CLOSED OVEN**	low (so long as the temperature does not exceed the safety limit – see above for details)
Total solvent volume	Explosive capability	**ALL WORK MUST BE CARRIED OUT IN A CLOSED OVEN**	low (so long as the total volume does not exceed the safety limit – see above for details)

Additional control measures to minimise residual risks	Implementation date

Who may be harmed			
Staff / students	☒	Cleaners / Engineers	☐
Supporting staff	☐	Others (specify):	

Emergency procedures – describe the response(s) required by the user and lab members
The bomb should be checked regularly for any signs of damage/ cracks. If there is any sign of damage, the bomb should not be used until either repaired or replaced. If an explosion occurs (due to overfill of the bomb) then the explosion should be contained within the oven, and should not result in the harm of those working in the area.

Recommended trainings and records:

List of individuals competent to demonstrate safe work practice and train others (level 1 trainers):	Names of those that have been trained and can work unsupervised (level 2) and date training completed:
1. Andreas Kafizas	1. Andreas Kafizas
2.	2. Elan Mistry
3.	3. Guangmeimei Yang 01/2021
4.	4. Paransa Alimard
5.	5. Oyelusi Olaifa
6.	6. Shize Li
7.	7. Akshi Gupta 21/02/2023
8.	8.
9.	9.
10.	10.
11.	11.