CVD REACTORS - RISK ASSESSMENT AND STANDARD OPERATING PROCEDURE

1. PERSON CARRYING OUT ASSESSMENT					
Name	Dr. Andreas Kafizas	**Position**	Junior Research Fellow	**Date**	10/07/2017

2. DESCRIPTION OF ACTIVITY (include storage, transport and disposal if relevant)

Setup, use of and deconstruction of 4x solid state heater unit for flow chemistry, comprising:

- 4x two-wire AC cartridge heaters inserted inside individual aluminium blocks (& clipped to an insulating board) for the purposes of heating an amount of fluoropolymer tubing.
- A Raspberry Pi configured as a Proportional Integral Derivative (PID) controller and 4x mains relay housed in a purpose built enclosure to control power to the above cartridge heaters and thereby provide invariant temperature control to said fluoropolymer tubing.
- A K-type thermocouple mounted on the outer surface of the aluminium block to provide an accurate surface temperature measurement for the PID controller.
- A multiplexed thermocouple data logger for digitising 4x thermocouples, and connected to RPi.
- An amount of fluoropolymer tubing whose properties are appropriate, and safe for the required operating temperature and pressure.
- A protective shield/cover for the purposes of preventing burns and chemical spills reaching the heat source.

3. LOCATION					
Campus	SK	**Building**	Chemistry	**Room**	541, FC 507 B

4. HAZARD SUMMARY			
Accessibility		**Mechanical**	
Manual Handling		**Hazardous Substances**	Chemicals and gases that will be carried into the reactor are covered by separate COSHH assessments for each reaction.
Electrical	Mains power	**Noise**	
Working at height		**Extreme temperature**	Not extreme, but up to 550 C.
Falling objects		**Pressure/steam**	All reactions conducted at atmospheric pressure.
Trip hazards		**Other**	Use of glassware
Lone Working Permitted?	**Yes** ☐ **No** ☒	**Permit-to-Work required for planned maintenance?**	**Yes** ☒ **No** ☐ **N/A** ☐

5. Who might be harmed and how?			
Staff / students ☒	Reactor poses a burn risk by skin contact. Failure of the cartridge heater may lead to shorting on the carbon heat block, which without engineering controls, would present an	**Cleaners, engineers etc** ☐	

	electrocution risk. Chemical spill onto or near the heat source may lead to a fire if the auto-ignition temperature of the chemical/solvent is lower than the temperature of the heater.		
Support staff ☐		**Other**	

6. How often is the process being carried out?
Once a day ☒ Once a week ☐ Once a month ☐ Every 6 months ☐ Annually ☐ Other – give details

7. Brief description of the procedure	**Existing precautions (Controls)**	**Is risk high, medium or low?**
<u>Temperature control box</u>  front side  back side	A Eurotherm proportional–integral–derivative (PID) temperature controller (model 3216) is used to control the temperature inside the reactor [front side – left panel]. It applies electrical power to a cartridge heater, housed inside a carbon block, inside the reactor (see the next section on the reactor for more details). The Eurotherm controller monitors the temperature via k-type thermocouples [back side – right sockets]. One thermocouple is connected to the Eurotherm controller, another is connected to a Tempatron temperature control unit [front side – right panel]. The Tempatron controller limits the maximum temperature the reactor can reach, in the case the Eurotherm controller fails. If either thermocouple fails, no heating is applied by the temperature control box (a safety measure that is an automated process). The temperature control box is powered by the mains (230 V) [back side – middle socket]. The electrical components inside the box are shielded by the metal casing. Electrical components inside the control box are earthed, to the sides of the metal casing. The control box is in a raised position, on a lab-jack, to avoid short-circuiting, in the case of a solvent spill inside the fume hood (*e.g.* may occur due to user error when attempting to load the flask with a liquid precursor). The control box has been electrically tested by Mr. Stefanos Karapanagiotidis. He has highlighted that the “The plug at the end of the heating element is the IEC type mains lead, which although is for mains use, someone could use the heating element directly to a mains socket with the use of an IEC mains plug bypassing the controller by mistake.” USERS SHOULD BE SURE TO PLUG THE CARTRIDGE HEATER INTO THE TEMPERATURE CONTROL BOX [BACK SIDE – LEFT SOCKET], AND NEVER DIRECTLY INTO THE MAINS. NO MODIFICATIONS ARE PERMITTED WITHOUT CONSULTING THE ELECTRICAL SAFETY OFFICER PRIOR TO COMMENCING WORK	low

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<u>Setting the temperature control box</u>

level setting code

set-point high set-point 1

heating rate maximum power

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The Eurotherm controller, on the temperature control box, can be programmed, so that the user can control the rate at which the reactor is heated, the temperature it will reach, and how long it will stay at that temperature.

To do this, the user must go to the level 2 setting [level setting] and hold the bottom left button [] until the level options show, and then cycle using the second from left button [] to reach level 2. The Eurotherm will ask for a code number, use the up/ down buttons to select CODE 2 [code].

Once inside level 2, cycle to the option SPHI [set-point high], and select the maximum permissible temperature. In the example shown, the reactor has been set to reach a maximum permissible temperature of 400 °C.

To select the temperature you want the reactor to reach, cycle to SP1 [set-point 1]. In the example shown, the reactor has been set to reach 400 °C.

NOTE: YOU CANNOT SET A SET-POINT TEMPERATURE THAT IS HIGHER THAN THE MAXIMUM PERMISSIBLE TEMPERATURE, SET-POINT HIGH.

The rate at which the reactor heats to this temperature can be controlled using the SP.RAT option [heating rate]. In the example shown, the reactor has been set to heat at a rate of 9 °C per minute.

NOTE: USE CARE WHEN SELECTING THE HEATING RATE, IF YOU HEAT THE REACTOR TOO QUICKLY, GLASS SUBSTRATES CAN CRACK (>15 °C/ MIN, THE CHANCE OF CRACKING IS HIGH).

The maximum output of the cartridge heater can be controlled during this programme using the OP.HI function. In the example shown, 80 % has been selected, which limits the heating output of the cartridge heater to 80 % of its maximum power (750 W).

To start the procedure, hold the up and down buttons together. You can then use the up/ down buttons to select one of three options: (i) AUTO, (ii) OFF or (iii) MANUAL. Select the option AUTO to run the programme detailed above. Select the OFF option to turn the reactor off. Do not use the manual option.

NOTE: THE REACTOR WILL NOT HEAT IF THE TEMPATRON CONTROLLER IS SET TO A TEMPERATURE LOWER THAN THE ACTUAL TEMPERATURE. THIS SERVES AS A SAFETY HEATING LIMIT ON THE REACTOR. IT IS ADVISED THAT THIS BE SET AT A VALUE 10 % HIGHER THAN THE TEMPERATURE YOU WISH TO REACH.

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<td><u>Reactor</u></td>
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The chemical vapour deposition reactor consists of two metal flanges, separated by a quartz tube [reactor]. O-rings are placed between each set of metal flanges to achieve a gas tight seal. Screws are used to hold the metal flanges in place, which can be tightened using the appropriate alum key.

NOTE: THESE SCREWS SHOULD BE LUBRICATED REGULARLY USING THE COPPER-BASED LUBRICANT

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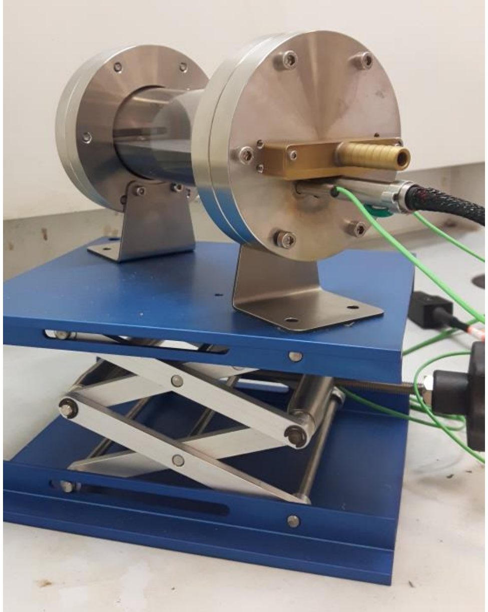
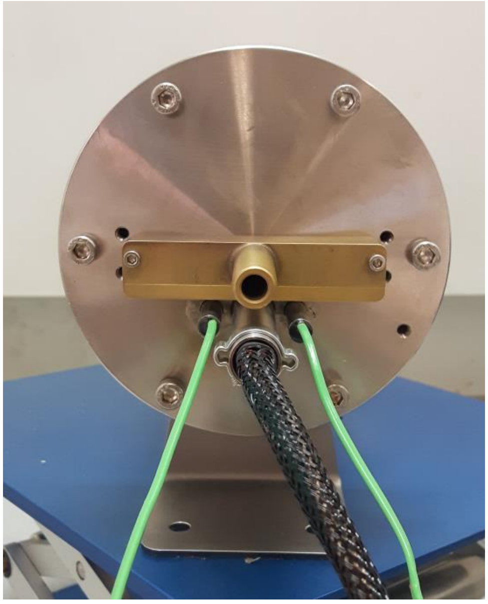
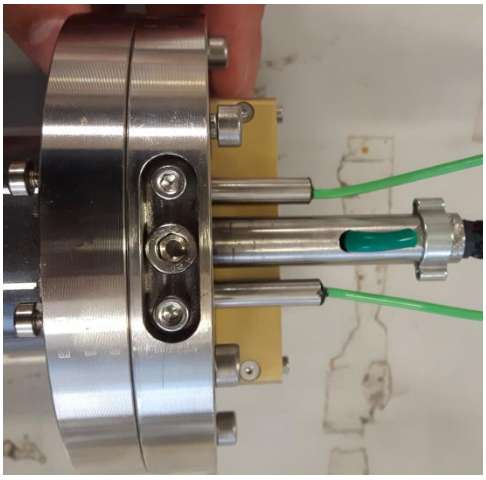


reactor



reactor – front view



reactor – bottom view of front flange

PROVIDED.

A hemi-cylindrical graphite carbon block sits inside the quartz tube. This carbon block has a cartridge heater inserted in its core, and two k-type thermocouples placed either side of the cartridge. The carbon block is the bed where reactions take place, on substrates that are placed on top of this flat, heated surface (such as FTO coated glass, barrier glass and metal plates *e.g.* Ti or steel).

The CVD reactor is on a raised lab jack stack. This has a two-fold purpose: (i) to avoid coming into contact with any accidental solvent spills and (ii) to adjust the height for connections to the gas stream, which carriers the precursors into the reactor via the baffle manifold [reactor, brass inlet at front]

Rubber pads are attached to each of the two flange supports to inhibit the reactor from slipping on the lab-jack.

The cartridge heater (750 W, firerod), and two k-type thermocouples, are connected to the temperature control unit (see above section for more details). Given the power of the cartridge heater, the reactor cannot go above 550 °C.

After electrical testing by Mr. Stefanos Karapanagiotidis, he has highlighted that,

"The heating element is deteriorating on a low level, possible caused from the enclosed pipe casing."

THEREFORE, THE STATE OF THE HEATER MUST BE PERIODICALLY ASSESSED ON A BI-ANNUAL BASIS.

Additional metal piping has been attached to the front fact of the reactor, where the cartridge heater is inserted [reactor – bottom view of front flange]. This is to ensure that the wiring on the cartridge heater is not tampered with. An earth wire runs alongside the live and neutral wires of the cartridge heater, which are encased within a braided polymer casing [reactor – front view].

THE INTEGRITY OF THE BRAIDED CASING WILL BE REGULARLY ASSESSED. IF ANY WIRING BECOMES EXPOSED, THE BRAIDING MUST BE REPLACED BEFORE THE UNIT IS USED.

Each wire is individually insulated within silicon casing. The earth wire is connected to the extended metal piping by a crimped metallic clip [reactor – bottom view of front flange].

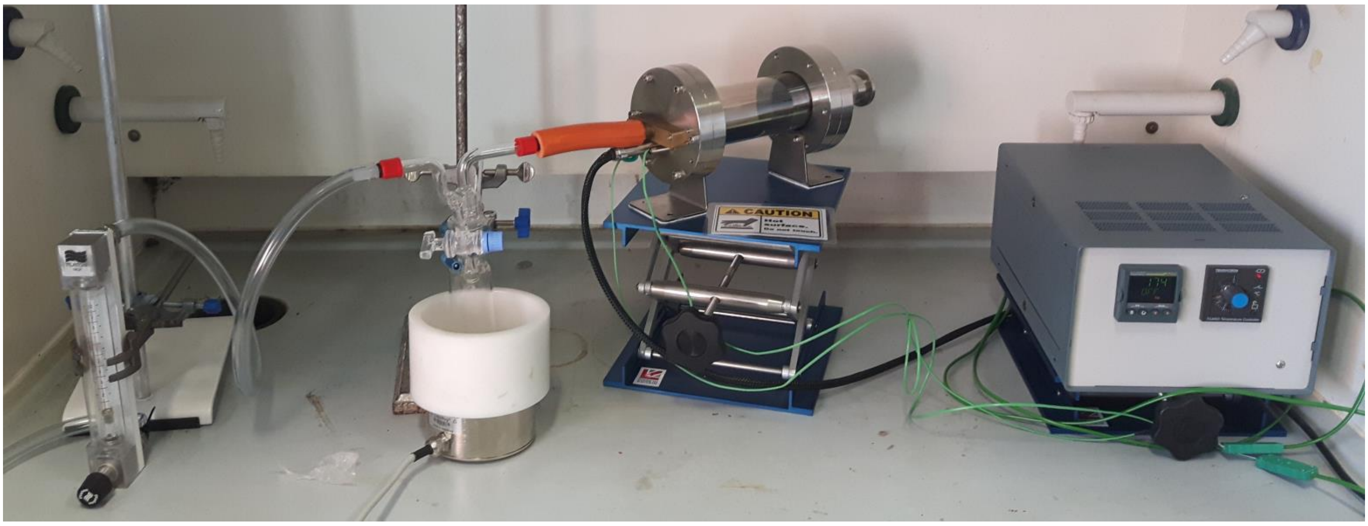
THE INTEGRITIY OF THE CRIMPED CLIP, AND CONNECTION TO THE EARTH WIRE, WILL BE REGULARLY ASSESSED BEFORE USE. IF THE CONNECTION BECOMES LOOSE, THE CONNECTION MUST BE REPAIRED BEFORE THE UNIT IS USED.

Each thermocouple is held in place by a grub screw, allowing for easy replacement of a faulty thermocouple.

NOTE: the temperature control unit does not supply power to the cartridge heater upon detection of a faulty thermocouple.

THE REACTOR CANNOT BE USED OUTSIDE OF THE FUMEHOOD. WHEN THE REACTOR IS IN OPERATION, THE "CAUTION! HOT SURFACE" SIGN SHOULD BE POSTED ON THE FUMEHOOD SASH TO WARN OTHERS THAT THE REACTOR IS HOT AND A POTENTIAL ELECTRICAL HAZARD. THE FUMEHOOD SASH MUST BE KEPT LOW WHEN THE REACTOR IS

<table>
<tr><td></td><td>IN OPERATION.

NO ADDITIONAL EXPERIMENTS MAY BE PERFORMED IN THE FUMEHOOD, AS THE USE OF SOLVENTS MAY RESULT IN AUTO-IGNITION FIRES. THIS FUMEHOOD IS DESIGNATED FOR THE SOLE PURPOSE OF CHEMICAL VAPOUR DEPOSITION CHEMISTRY.</td><td></td></tr>
<tr><td colspan="3"><u>General operation</u>

standard arrangement of apparatus</td></tr>
<tr><td></td><td>First check that the area is clean and clear. In general, all apparatus should be kept at least 15 cm away from the front of the fume hood.

Check that the reactor is cool (i.e. at around room temperature) before handling it (you can do this by turning on the temperature control unit, which will give you a temperature read-out). This also serves as a check to see if the temperature read-out from the thermocouple is correct. The last user should also have set the Tempatron controller to a temperature below zero (i.e. at around room temperature) no heating can be applied).

If the reactor is sufficiently cool (i.e at , load your substrate into the reactor from the exhaust end (you can do this by unscrewing the six screws from the flange at the back of the reactor).

Check that the thermocouples and cartridge heater are securely attached to the reactor.

Make sure that the cartridge heater is secure in the heat block and that the earth wire is connected to the heat block.

Ensure all cables are attached to the temperature control box; in their correct positions (see the temperature control box section for more information).

Before heating the reactor via the temperature control box, ensure that all wiring and cables are not touching the reactor.

Check that the set point temperature of is suitable for the reaction. Also check that the Tempatron safety limiter is set to a temperature roughly 10 % higher than the temperature you wish to reach.

Connect the PVC tubing from the gas cylinder, to the flask, to the inlet of the reactor.

Purge the reactor with the carrier gas you will use during your deposition, whilst the reactor heats up. Use a trickle flow of gas to be economical.</td><td>low</td></tr>
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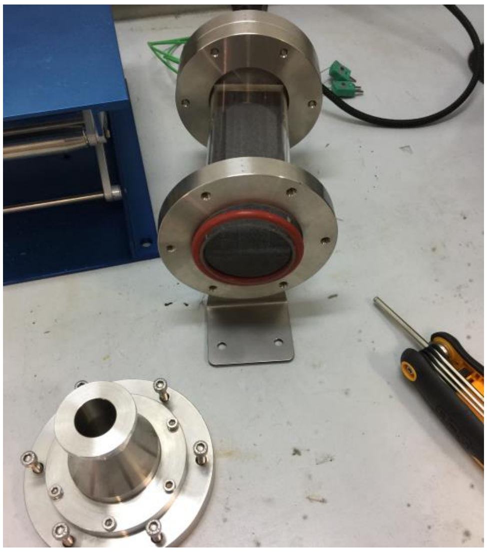
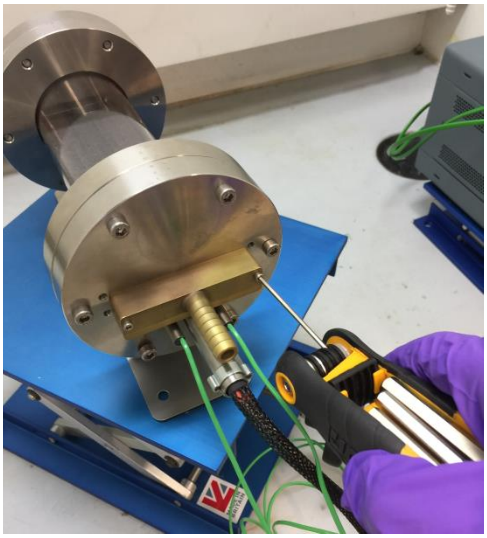
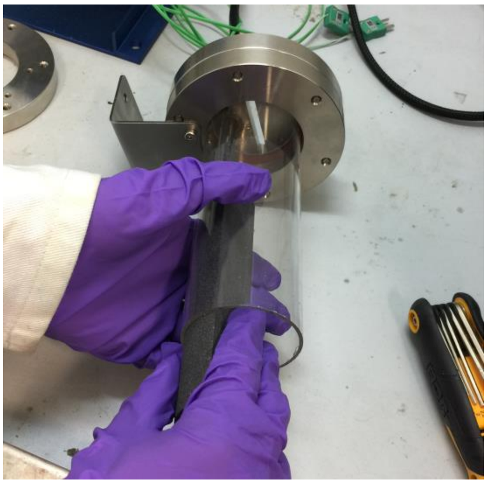
	When your reactor reaches temperature, inject the precursor solution into the flask, *via* the side-arm. Then turn on the ultrasonic humidifier to excite the solution and create a mist. Now turn the gas flow up to the desired flow rate. Continue the reaction until the flask is empty, and then turn the ultrasonic humidifier off. You can turn off the heat to the reactor *via* the temperature control box, by first turning off the procedure and then setting the Eurotherm to OFF mode (see setting the temperature control box section for more information). Then turn the Tempatron controller to below zero to ensure no further heating is applied to the reactor. Note that you will need a separate COSHH form for the precursors and solvents you will use – evaluate the risk of the precursors and solvents you intend to use and the associated risks when carried into a heated reactor. <u>SOLVENT SPILLAGE</u> THE ULTRASONIC HUMIDIFER REQUIRES WATER TO OPERATE. DO NOT FILL ABOVE HALF-WAY TO AVOID SPILLAGE. IN THE CASE OF MINOR SPILLAGE, MOP UP IMMEDIATELY. IN THE CASE OF SEVERE SPILLAGE, AND POSSIBLE WETTING OF ELECRONICS OR CABLES, TURN OFF ALL ELECTRONICS FROM WALL PLUG BEFORE TACKLIING THE SPILL <u>FIRE RISK</u>. EACH DEPOSITION REACTION HAS AN ASSOCIATED COSHH FORM. THERE IS NO RISK OF FIRE IF THE PROCEDURES OUTLINED ABOVE ARE STRICKTLY ADHERED TO. HOWEVER, IN THE CASE THAT USER MAY MISTAKENLY INJECT THE PRECURSOR SOLUTION DIRECTLY INTO THE REACTOR, OR SPILL THE SOLUTION ONTO THE REACTOR, A FIRE MAY RESULT DUE TO THE AUTO-IGNITION TEMPERATURE OF THE SOLVENT BEING SURPASSED (*e.g.* ACETONE = 465 °C, METHANOL = 470 °C, HEXANE = 235 °C *etc*) IN THE RESULT OF A FIRE, TURN OFF ALL ELECTRICAL EQUIPMENT FROM WALL PLUG, GAS FLOW FROM CYLINDER HEAD AND CLOSE THE FUMEHOOD SASH. IF ADEQUATELY TRAINED, TACKLE THE FIRE USING THE CO_2 EXTINGUISHER (LOCATED OUTSIDE OF THE LAB, TO THE LEFT IN THE CORRIDOR). SOLVENTS MUST NOT BE STORED INSIDE THE REACTOR TO AVOID THE SPREADING OF A POTENTIAL FIRE. IN THE CASE THAT THE CENTRAL QUARTZ CYLINDER CRACKS, DUE TO POOR HANDLING, REPLACE IMMEDIATELY. THE USE OF A CRACKED QUARTZ CYLINDER IS NOT PERMITTED. ENSURE THAT THE TEMPATRON CONTROLLER IS SET TO ZERO WHEN THE REACTOR IS NOT IN USE.	
<u>Shutdown</u>	DO NOT SWITCH OFF THE TEMPERATURE CONTROL BOX. Instead, set the Eurotherm to the OFF setting, and allow the heating block to cool down naturally (see setting the temperature control box for more details). Heating can also be stopped by turning the Tempatron control temperature to below zero. This will automatically	low

	stop power being delivered to the cartridge heater. Keeping the temperature control box on will serve as a reminder that the heat block is hot while you are clearing up, and serve as a warning to other lab users that the heater is hot. The reactor should be purged with carrier gas flow on cool-down, to ensure the complete release of all aerosols from the reactor. A trickle flow will suffice, to be economical.	
Cleaning and maintenance  loading/ unloading samples  baffle manifold – detachment	BEFORE HANDLING THE REACTOR, MAKE SURE THAT THE REACTOR IS COOL (*I.E.* AT ROOM TEMPERATURE), THE GAS FLOWS ARE TURNED OFF FROM THE CYLINDER HEAD, AND THE ELECTRONICS ARE TURNED OFF FROM THE PLUG. CABLES ATTACHED TO THE TEMPERATURE CONTROL BOX SHOULD BE DETACHED (CARTRIDGE HEATER AND TWO THERMOCOUPLES). GAS-LINE TUBING SHOULD BE DETACHED. THE REACTOR SHOULD BE DISASSEMBLED WITH WITHIN THE FUMEHOOD. THE REACTOR SHOULD NEVER BE PICKED UP FROM THE QUARTZ TUBE. INSTEAD IT SHOULD BE HELD FROM THE TWO OPPOSITE FLANGES. All screws can be undone using hexagonal keys. Between each deposition reaction, the user will unload/ load their substrate. The reactor chamber, where the substrate is loaded, can be accessed most easily from the exhaust flange [loading/ unloading samples]. The user should undo the 6 outer screws to remove the exhaust flange to load/ unload their substrate. NOTE: THE O-RING CAN DETERIORATE OVER TIME AND SHOULD BE REPLACED IF WORN. After a typical chemical vapour deposition reaction, the reactor with accumulate powdery deposits on the inside of the quartz tube, the exhaust flange, and can clog the baffle manifold. The baffle manifold must be free from powdery deposits to avoid blockage during depositions, and should be cleaned after every other deposition. The baffle manifold can be detached by unscrewing two screws on the front face [baffle manifold – detachment]. The baffle manifold can be best cleaned by removing the bottom plate, by removing the two screws on the underside of the baffle [inside the baffle manifold]. ALL NON-ELECTRICAL REACTOR PARTS SHOULD BE CLEANED IN TWO STAGES: (I) A QUICK WIPE WITH WET BLUEROLL TO REMOVE	low

inside the baffle manifold



removing the carbon block

replacing thermocouples

MOST OF THE POWDERY DEPOSITS. DIRTIED BLUE-ROLL SHOULD BE DISPOSED OF IN THE DESIGNATED CLINICAL WASTE BIN

(II) CLEANED MORE THOROUGHLY WITH TEEPOL, A SPONGE AND RUNNING WATER IN THE SINK.

FOR TOUGHER STAINS, PARTS CAN BE SONICATED IN THE SONIC BATH WITHIN A FUMEHOOD TO AVOID CREATING HAZARDOUS VAPOURS.

The carbon block can be removed by sliding the block out of the reactor [removing the carbon block]. The carbon block is brittle, can easily crack, and should be handled with care. Removing the carbon block exposes the cartridge heater and two thermocouples.

A faulty thermocouple can be easily replaced, by unscrewing the grub screw that holds it in place, accessed from the underside of the inlet flange [replacing thermocouples]. Replacing a faulty cartridge heater is a more difficult process (as it involves detaching the safety earth wire that is crimp clipped to the extended metallic support cylinder).

THE CARTRIDGE HEATER SHOULD NOT BE REPLACED BY THE USER, AND SHOULD BE TAKEN TO THE ELECTRICAL SUPPORT TECHNICIAN MR. STEVE ATKINS TO BE REPLACED.

The quartz tube is fragile, can easily crack, and should be handled with most care. It is also a rolling hazard, and can potentially roll off the edge of a work bench and smash. For this reason, all cleaning and maintenance should be carried out in the fumehood.

The quartz tube has been polished at the ends so that it is less sharp. However, with use, the tube can chip at the edges where it is clamped to the support flanges. Chipping makes the quartz tube sharper at the ends, and also, more liable to crack.

USE THICK GLOVES WHEN HANDLING THE QUARTZ TUBE TO AVOID CUTS. REPLACE A CRACKED TUBE IMMEDIATELY. DO NOT USE A CRACKED QUARTZ TUBE FOR DEPOSITIONS.

9. EMERGENCY ACTIONS

In the event of fire: raise the alarm using the red alarm boxes, if trained and comfortable doing so apply one (and only one) CO_2 fire extinguisher to the fire. Try to isolate electrical equipment if possible to limit secondary fires. Evacuate the lab and shut the door. Evacuate through main entrance, and find a fire officer.

In the event of electrical burn: apply cold water to the burn and see first aid immediately. Report incident by SALUS within 24 hours.

In the event of heat burn: apply cold water to the burn and seek first aid immediately. Report incident by SALUS within 24 hours.

Specific emergency actions for exposure to chemicals in the flow reactor experiment should be found in the COSHH assessment.

Generally:

In the event of skin contact: without contaminating other areas immediately wash contact area with copious water and rinse hands for c.a. 15 minutes. Report incident via SALUS within 24 hours.

In the event of cut: run cut under warm water for 10 minutes to encourage bleeding (flushes the wound out rather than sealing the wound). Then, apply cold water for 15 minutes to stop bleeding. Seek first aid assistance. Report incident via SALUS within 24 hours.

10. Monitor and review

Controls should be monitored: daily ☒ weekly ☐ monthly ☐ 6 monthly ☐ annually ☐ other☐

I will review this risk assessment at least every 6 months ☐ every 12 months ☒

Immediately in the event of process / location change or incident or accident

11. Training record – use this section to record the names and date of any persons you are training in this risk assessment and associated procedures

Name	Date	Name	Date
Dr. Andreas Kafizas	11/07/2017		
Mr. Xinyi Shen	11/07/2017		
Mr. Ruohao Li	17/07/2017		
Mr. Zachary Feng	08/02/2023		
Bowen Du	08/02/2023		
Zhipeng Lin	13/02/2023		
Longren Li	09/02/2023		
Tristan McCallum	13/02/2023		

Note: http://www3.imperial.ac.uk/safety/formsandchecklists/raforms1 for specific risk assessment forms and guidance
http://www3.imperial.ac.uk/safety/guidanceandadvice on gases, biological agents, chemicals, offsite work etc

Despite my recommendations for improvements to this design to make this unit safe for use in experiments, some of the changes I think necessary have not been included in the design, so the unit falls below the standard recommended by the HSE and IET.I therefore cannot pass this unit for use in its present condition.

However if the PI would like to write something to take full responsibility for any problems occurring with the use of this unit by the researchers then it can be released.