ATR-FTIR Modulation Excitation System

Standard Operating Procedure

Lab: 270 Davenport

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Section 1: Overview

Type of SOP: ☒Process ☒Hazardous Material ☐Hazardous Class of Materials ☒Equipment

Synopsis:

This SOP is designed to provide directions for using the ATR cell in the Vertex FTIR system

Section 2: Risk Assessment Summary (Hazards and control measures)

Information obtained from performing a risk assessment should be entered into this section.

Materials:

Material (name, CAS #, other ID)	Hazards
Hydrogen	Flammable, asphyxiant
Carbon Monoxide	Toxic, flammable, asphyxiant
Helium	Asphyxiant especially at high pressures
Oxygen	Oxidizer, Explosive in mixtures with H_2

Relevant References for Material Hazards:

Hydrogen—Airgas,
http://airgas.com/msds/001026.pdf

Carbon Monoxide—Airgas,
https://airgas.com/msds/001014.pdf

Oxygen – Airgas,
https://www.airgas.com/msds/001043.pdf

Helium
https://www.airgas.com/msds/001025.pdf

Propylene Oxide
Please see addendum “PO SOP” in Group SOP folder

Equipment Hazards:

Variacs and heating tape—Ignition source, electric shock

Glass Syringe needles—Sharps hazard

Crystal Polisher: Ignition source, electric shock, pinch hazard

Legato Syringe pump—electric shock

Gas lines—High pressure system, hot surfaces

Mass Spectrometer – electric shock, hot surfaces

Series HPLC Pump – electric shock, spill hazard

Hazardous Conditions:

Pure Hydrogen and pure oxygen is fed to the liquid in the saturator. Care should be taken that these gases never come into contact with each other

CO is toxic. Flow in diluted concentrations. Keep lab mates aware any time CO is in use. Check the CO detector batteries prior to starting any flow. When CO is used in the cell, the outlet from the cell should be connected to the mass spectrometer (which is vented) or the vent line. The sash should be completely down with panels closed as always.

High temperatures can be reached by heating cartridges. Stay near system during initial heating. Post signs to indicate hot areas

Technique Hazards:

None

Personal Protective Equipment

Wear cold thermal gloves (blue) to avoid burns when filling detector or probe with liquid nitrogen.

Wear warm thermal gloves to avoid burns from heated cell or transfer lines.

Wear appropriate nitrile (or other) gloves when handling liquid reactants.

Wear safety glasses at all times when operating system (i.e. any time in lab setting…).

Engineering Controls

3% CO in He is stored in the fume hood with a vent line to purge manually. Pure CO is stored in gas cabinet with pneumatic controls to avoid high flow rates. Valves on regulator system are Normally Closed if power is out or house air pressure is not high enough.

Watlow controller, heating cartridges, and variac are plugged into ground fault circuit interrupters, which will trip if current exceeds 15 amps. Fuse in Watlow controller will also blow at 15 amps in case of a short in the system or drawing too much current.

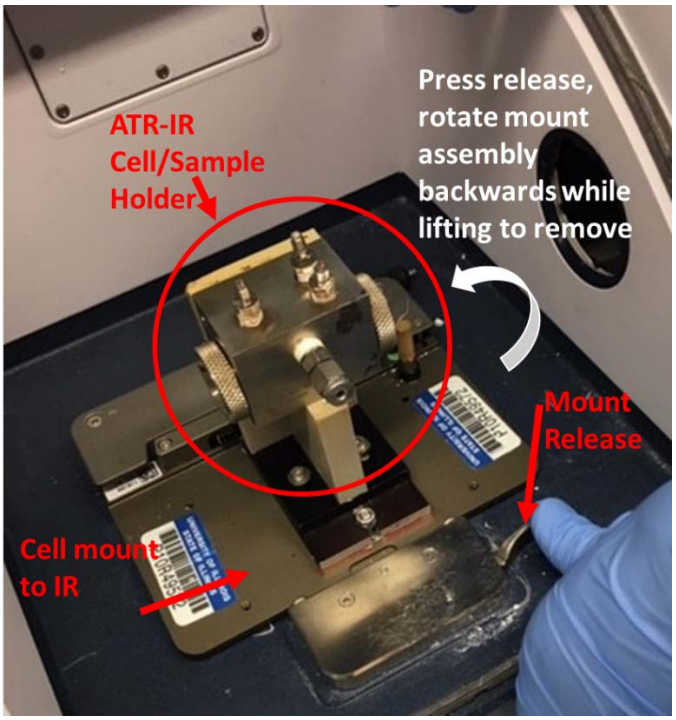
CO detector should be kept near IR compartment (close to MFCs). Check batteries prior to flowing CO.

Exit gases are piped directly to the back of the fume hood.

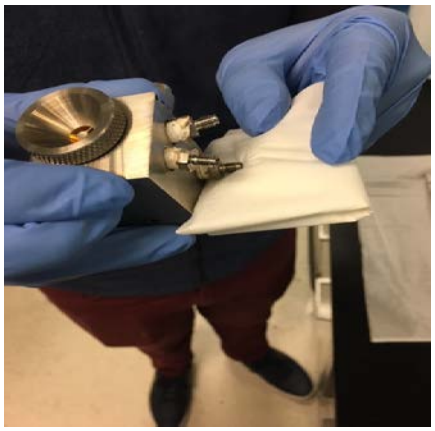
Section 3: Procedures

Removing the ATR crystal

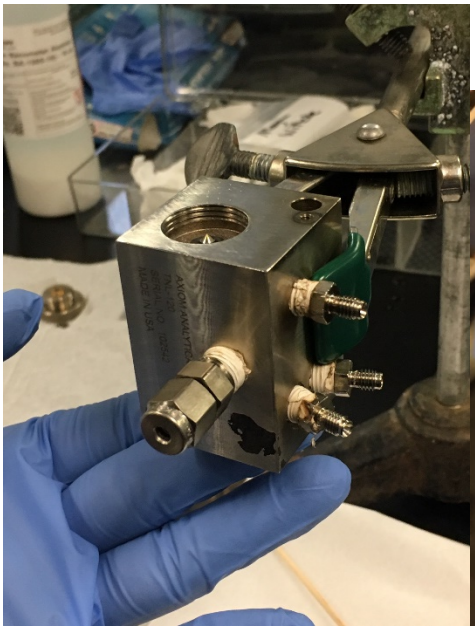
1) Remove the mounting assembly from the IR

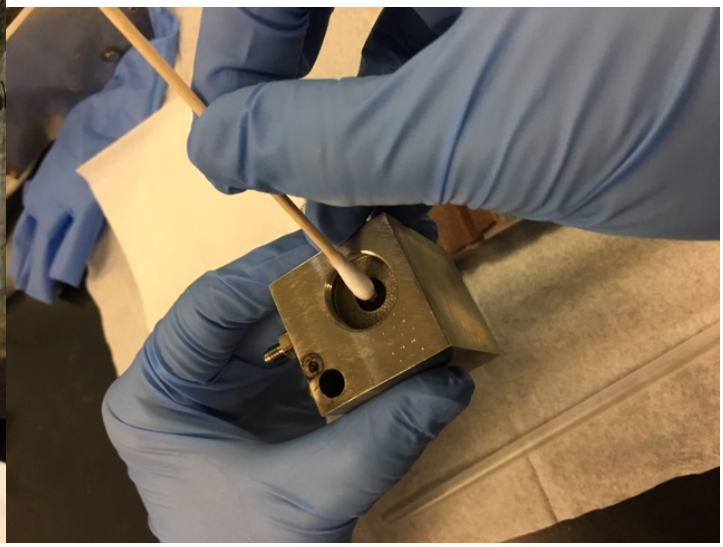


2) Remove the cell from the mounting assembly
3) Remove the end cap, gold cone, and spider from each end of cell
4) Drain any excess solvent from the ATR cell by holding inlet and outlet ports of cell against Kimwipe

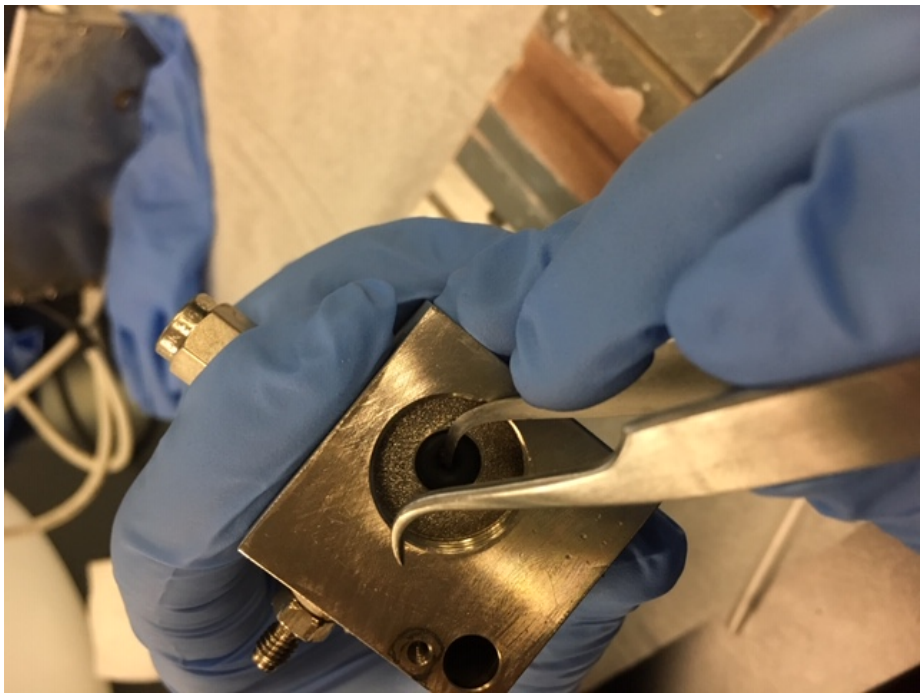


5) Place a piece of lens paper or soft tissue over one end of the ATR rod. By using the plastic rod insertion tool, gently press the rod out of the cell. As the rod is removed, the emerging end should be supported so as to avoid contact between the rod and cell body.





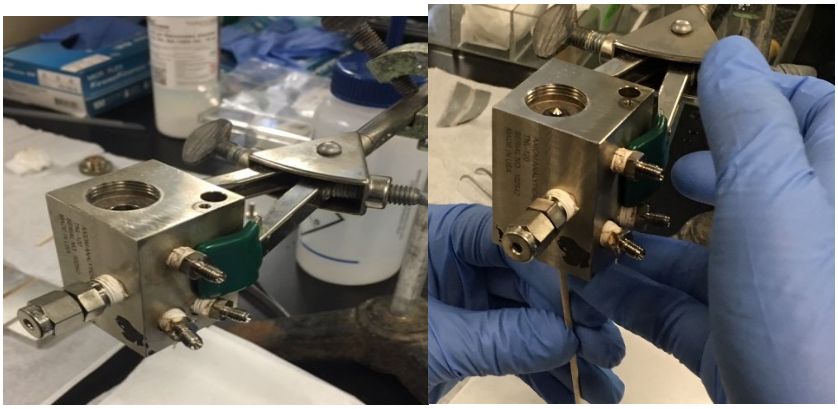
6) If the rod has been installed for a long time, it may not press out easily. In this case, it often helps to flood O-rings with a lubricating solvent such as acetone or water. It may also be necessary to use tweezers to remove O-rings or destroyed rubber bits



7) Clean the empty ATR cell by flushing with water and using a Q-tip the brush out any trace catalyst. Sonicate ATR cell for ~10 minutes, then rinse with DI H_2O followed by acetone, followed by drying in acetone oven for ~ 15 minutes.
8) Clean and polish the crystal using instructions below.

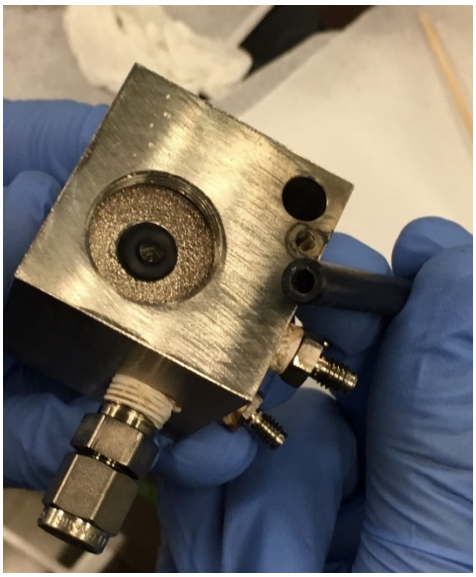
Inserting the ATR crystal into the cell

1) Gently place an O-ring on the ATR rod near one end.
2) While holding or clamping the cell body in a vertical orientation slide the insertion tool partway through the body from the bottom.



3) Carefully insert the ATR rod from the top using the insertion tool to keep it centered in the cell body.

4) Insert the second O-ring around the lower end of the ATR rod and use the O-ring seating tool to fully seat it. In doing this, you can press the rod from the top using a soft tissue to keep it approximately centered in the cell.

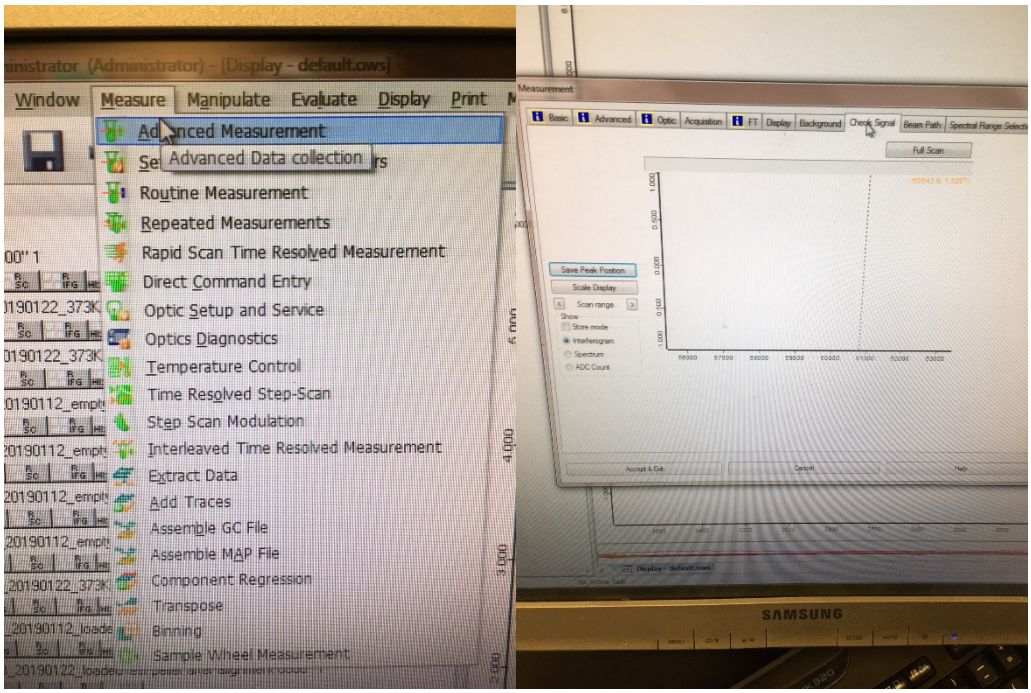


5) By alternatively using the rod insertion tool and the O-ring seating tool make sure that the rod is centered in the cell body and that the O-rings are fully seated in their pockets.
6) Reinstall the end caps, gold cones and spiders.
7) To check the centering of the ATR rod, compare the appearance of the rod as viewed from both ends. If a dark circle appears around either the inner or outer periphery of the optical aperture, the rod is not properly centered. A dark circle around the inner periphery indicates that the rod is too close to this end. In this case, remove the near end cap, spider and cone and loosen the far end cap slightly to allow the rod to move through the O-ring. Use the insertion tool (covered with a piece of tissue) to better center the rod.

Preparing the FTIR and Checking the ATR crystal

1) Make sure that the FTIR is switched on and the purge gas is connected. The three indicators on the FTIR (Laser, humidity, status) light should be green.
2) Fill liquid nitrogen in the FTIR to cool the detector. Fill until liquid nitrogen is seen coming out of the detector. <u>You need to wait ~20 min after filling before you take any spectra.</u>

3) Open OPUS and go to advance measurements. In advance measurements, open the check signal tab to see if there is signal being detected. The value of amplitude should be greater than 13,000 but less than 30,000. Adjust the gain of the background and aperture to 1x and 1mm respectively under 'Optics'.



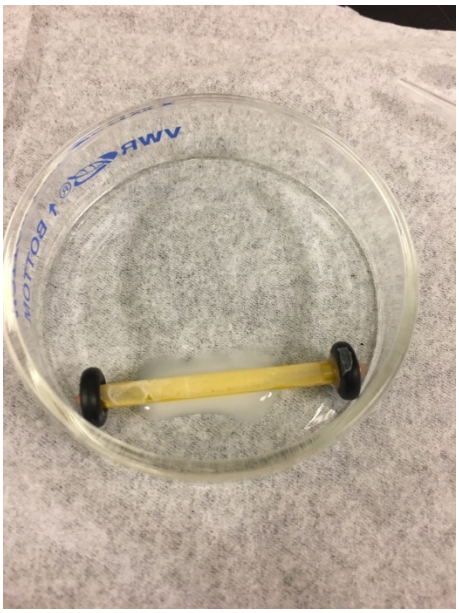
4) The 'Position' on the interferogram on the Check Signal tab should be ~59426 – this is the peak value in the interferogram. If the position is significantly different, check to make sure the detector is cooled and that nothing is in the beam path. This value should not drift over time. Next check that the scale includes 59000-60000. If you still don't see the interferogram signal, consult Bruker.

5) Take a background with empty compartment with the aperture set to 1 mm and a gain of 1x for the background.
6) Install the ATR accessory into the sample compartment carefully.
7) Again check the signal. The signal amplitude will decrease. Adjust the size of aperture (Advance measurements>>optics; will likely need 8 mm) and sample signal gain to get a value between 13000 and 30000. Strategy for changing aperture and gain: set gain to 1x and adjust aperture firs THEN adjust gain as needed.
8) Take a spectra recording the ***transmission*** of the polished crystal in the cell (with no catalyst applied to it). Transmission values depend on the crystal material (e.g., ZnSe vs. Ge). Keep track of the transmission values of each ATR crystal over time to see if you have polished the crystal well enough and to check the 'health' of the crystal.

Depositing catalyst on to crystal

1) Grind catalyst with mortar and pestle to a fine powder
2) Create slurry of catalyst and solvent (~roughly 1 mL solvent to 10-15 mg catalyst).
3) Sonicate briefly (~5 seconds) to suspend particles. You may need to repeat this during the deposition process.

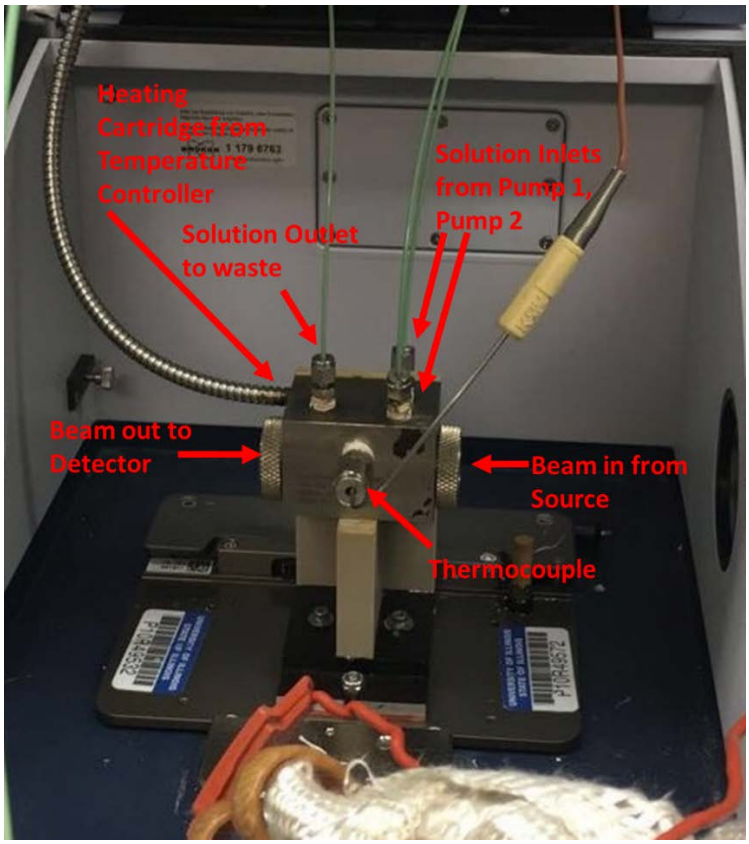
4) Remove ATR crystal from cell (following instructions above). *You need to be sure to check the transmission of the crystal before applying the catalyst to determine if more polishing is required.*
5) Put O-rings onto crystal ends (farther in than they would be when the crystal is in the cell). Place crystal into petri dish. Place petri dish on top of heating plate.

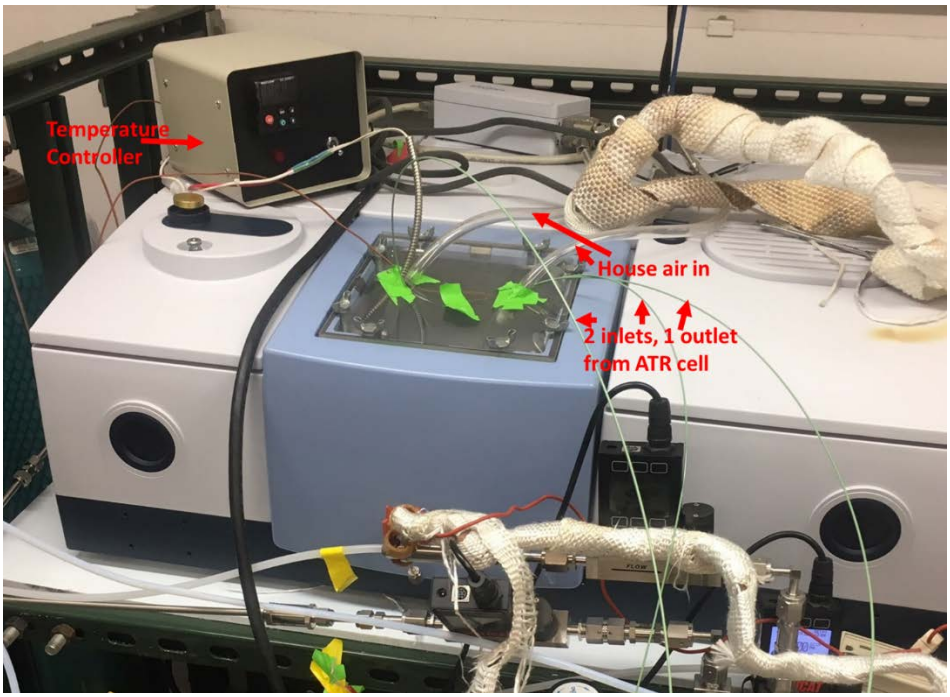


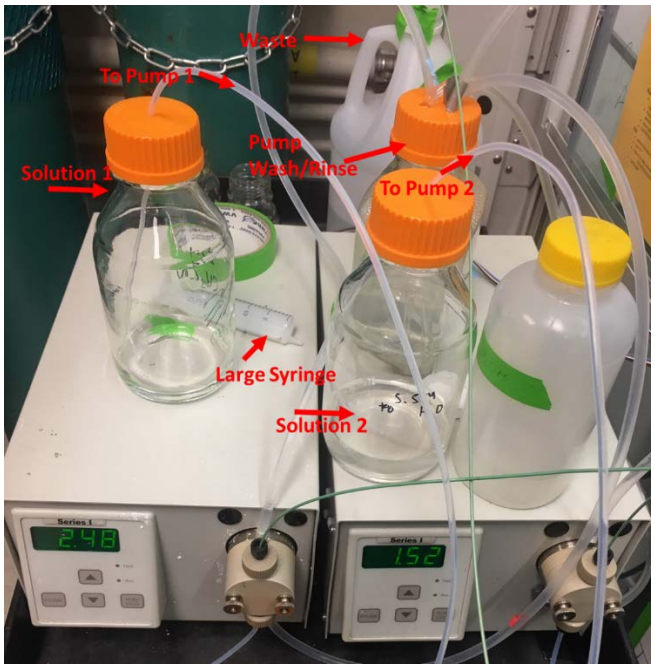
6) Set heating plate to low heating value (warm to touch, ~1 or 2)
7) Apply 1-2 drops of catalyst/solvent slurry onto center of crystal (between the O-rings).
8) Allow solvent to dry.
9) Repeat application of drops until a uniform coating of catalyst is over crystal. Carefully rolling crystal in petri dish may help spread slurry evenly as it dries.
10) Once the uniform coating is achieved, use CLEAN, NEW o-rings and insert crystal back into cell (using instructions above). Do not use the o-rings used during the deposition of catalyst as some catalyst will likely end up on the o-ring and ruin the seal in cell.

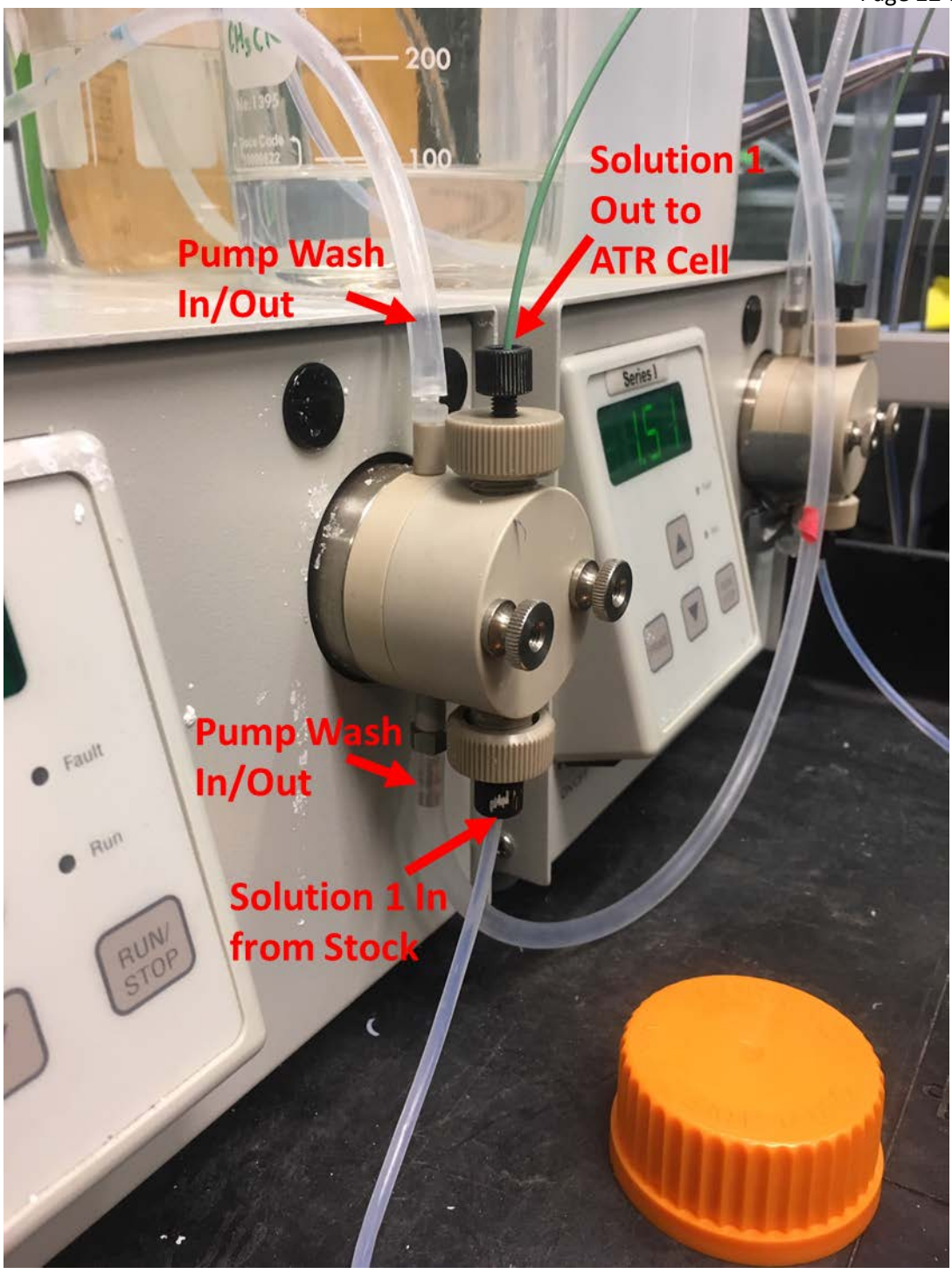
Running experiments

1) Insert ATR setup with cell and catalyst coated crystal back into IR sample compartment.
2) Adjust gain and check *Transmission* of coated crystal. Transmission below 2% will be very challenging to measure signals. Ideally, you'd like transmission greater than 10%.
3) Insert heating cartridge and thermocouple into ATR cell, and attach ground to ATR cell side screw.
4) Connect 1/16" tubing for inputs and outputs to the ATR cell. *You will want the sample compartment lid to be able to close during the experiment, so the tubing thermocouple and heating cartridge need to run through holes in the top of the sample compartment. Tape the holes in the top of the sample compartment to make sure they seal and the compartment is swept with purge gas throughout the experiment.* ***Note: Following pictures refer to liquid phase ATR-IR setup***


Heating Cartridge from Temperature Controller
Solution Outlet to waste
Solution Inlets from Pump 1, Pump 2
Beam out to Detector
Beam in from Source
Thermocouple


Temperature Controller
House air in
2 inlets, 1 outlet from ATR cell


Waste
To Pump 1
Pump Wash/Rinse
To Pump 2
Solution 1
Large Syringe
Solution 2



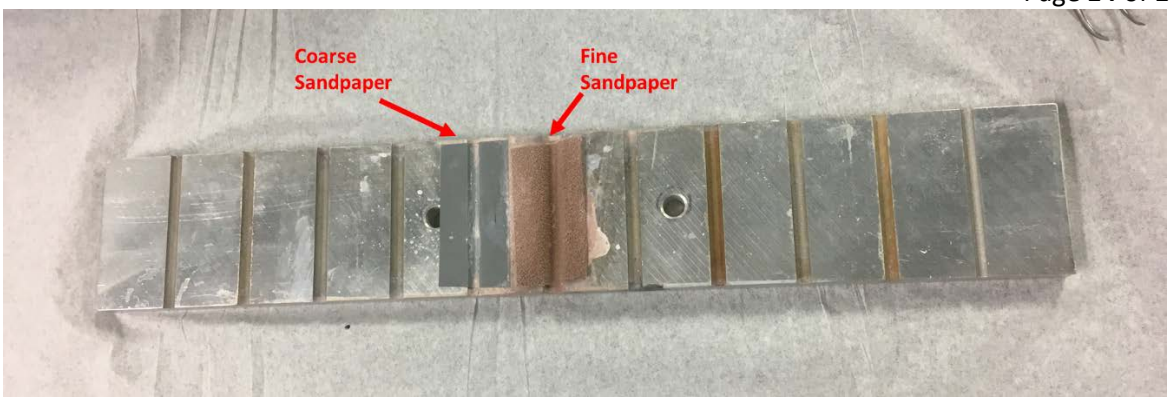
5) If flowing gas, leak check with He. If flowing liquid, flow the solvent without reactant (ideally the solvent you will pretreat with) and check for leaks.
6) The mass spectrometer can be used if running the system in gas phase, but NOT LIQUID. Follow SOP for Mass Spectrometer.

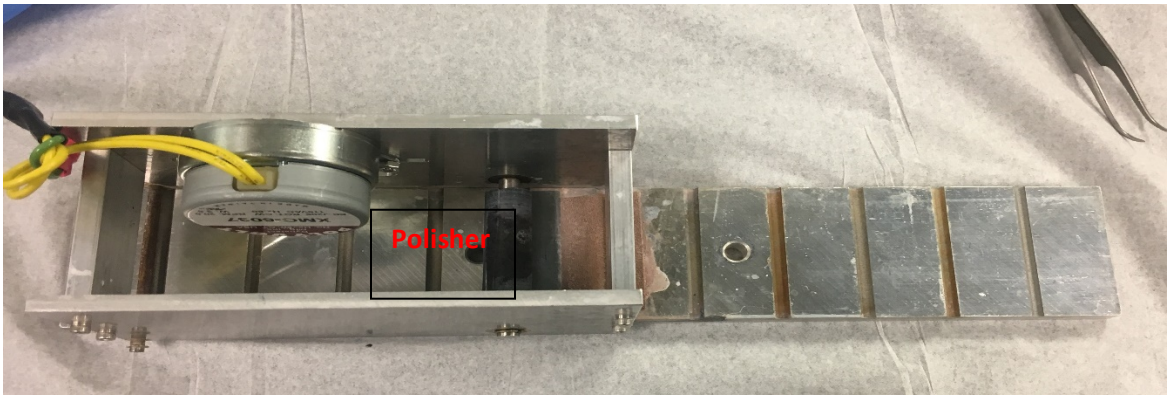
7) Liquid waste must be collected in a separate container that must be placed above the pump outlet. *All liquid reactants and methanol/water mixture used Series Pump must be stored to the right of the IR (NOT ABOVE) and in secondary containers to protect the mass spectrometer that is located on the first level.*

8) Go through any pretreatment procedures (e.g. priming pumps with solutions using large syringe). Set the flowrates on the pumps and/or MFCs. Use the Watlow controller to set the temperature and control ramp rates. Watch the temperature increase a few degrees before leaving setup to ensure everything is properly controlled.
9) After pretreatment, reach reaction temperature and flow solvent or He to take background spectra. Make sure wavenumber resolution is the same that you wish to use during experiments.
10) Begin experiments and measure *ABSORBANCE* not transmittance.
    a. Take note of signal regularly throughout the experiment. Certain conditions may change absorbance conditions enough that the gain needs to be adjusted.
    b. Control temperature carefully during experiments – drift will affect baseline.
11) When finished, stop flow, stop heating, and detach the 1/16" fittings, thermocouple, ground wire, and heating cartridge from the ATR cell. Remove ATR setup from sample compartment. Remove crystal (instructions above), clean and polish crystal (instructions below).
12) Save your data. Raw OPUS files can be converted to csv files in batches using the Macro 'OPUS_TO_CSV_BY_FOLDER.mtx'. Make a folder for the csv files to save into on the local computer. Move the raw files and the csv files to your folder on the group drive to back up your data and create free space on the local hard drive.
13) If using the Mass Spec, turn off filament when finished.

Polishing crystal

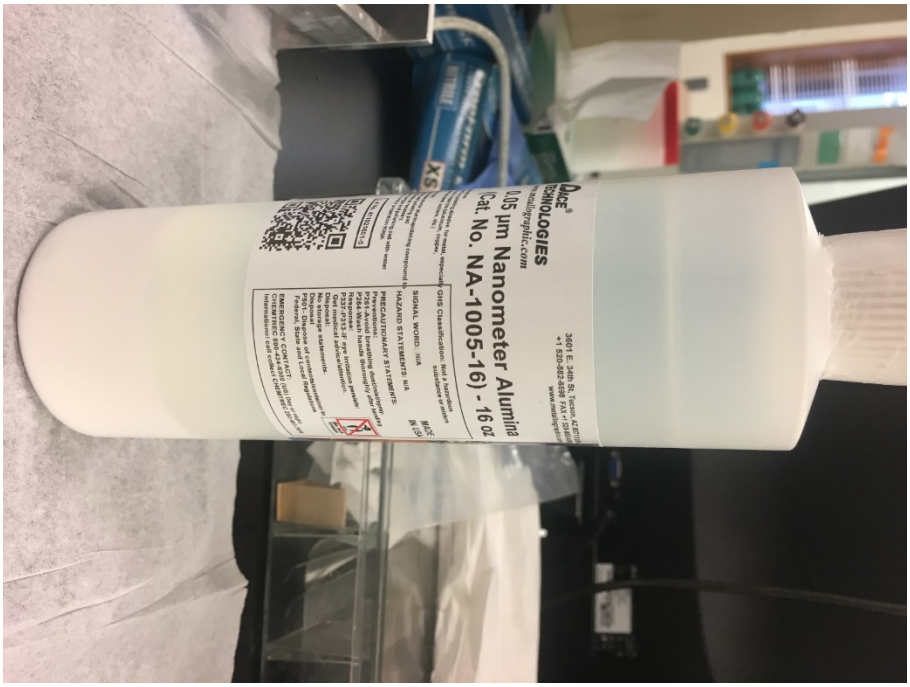
1) Wrap crystal in multiple Kim-Wipes. Sonicate in water for ~5min. Placing peetree dish upside down will stop the crystal-kim wipe bundle from floating and unraveling (and possibly breaking). ***Be very careful to protect the crystal at all times during this process.***
2) Set up polishing base with a new coarse polishing pad (the gray one). You will need to cut it to be narrower than the width of the polishing base. I found that the insertion tool is effective at pushing the pad firmly in to the semi-cylinder notches. Make sure the pad is well stuck to the base.



3) Add a small amount of water as a lubricant to the polishing pad and a few drops of water to the rubber polishing wheel.
4) Place the crystal in the center of the polishing pad, plug in the polisher –it will rotate immediately, but slowly. Carefully, set the polisher onto the base so that the rubber wheel aligns with the coarse polishing pad and lower the wheel to the crystal.
5) 

6) Check that the crystal is rotating with the wheel and that the crystal isn't sliding to hit the side wall of the polisher as it rotates. You will see the water turn slightly yellow for the ZnSe crystal because this step actually just grinds the crystal down slightly.
7) Regularly add water to the wheel/polishing pad. **If this process is not well lubricated with water, the crystal may become scratched.**
8) Polish with the coarse pad for ~30 min.
9) Stop the polisher. Sonicate the crystal (same as step 1) to remove the grit of the crystal you've removed.
10) The fine polishing pad does not need to be replaced every time you polish, so it will likely be attached to the polishing base already. If it is not or it needs to be replaced, apply a new fine pad (kind of a spongy material) to the base.
11) Place the crystal on the fine polishing pad. Shake alumina solution vigorously to homogenize solution. Apply 2-3 drops of alumina polishing slurry to the crystal. Note

that pH 10 is used for the ZnSe crystal, make sure that pH 4 solution is not used. *Note: pH 4 solution is marked "pH 4," while pH 10 solution is not marked.*



12) Apply 2-3 drops of water to the pad directly, so that it is moist. Apply a few drops of water to the rubber polishing wheel.
13) Set up the polisher so that wheel aligns with the fine polishing pad and carefully lower to align with the crystal.
14) Plug in polisher and check again that the crystal rotates but does not hit the polisher side wall.
15) Regularly apply a few drops of water to the rotating wheel. Add 1-2 drops of alumina slurry as needed. The alumina will get trapped in the pad, so sometimes just adding water is fine to keep the setup lubricated.
16) Polish for ~30-1hr.
17) Sonicate crystal to remove the alumina. (Again be very careful).
18) Load crystal into cell to check transmission (Instructions above).

NOTE: ***DO NOT LEAVE CRYSTAL ON POLISHER UNSUPERVISED!*** The setup may dry out causing the crystal to stick to the rubber wheel and cause problems when lifting the polisher away from the base (e.g., falling and cracking the crystal). The polisher may malfunction and slide the crystal off the base and roll to undesirable places. The crystals are expensive and should be handled with special care.

NOTE: Store crystals in the protective foam cases provided by the manufacturer to avoid damage.

Evacuating and re-pumping the MCT detector – Instructions are in the Vertex Manual

1) If the MCT detector lasts for less than 4 hours after filling liquid nitrogen, it is an indication of existence of water and contaminants inside the detector which needs to be evacuated.
2) Open the top panel of the FTIR and remove the detector by unscrewing one screw using the screw driver in Fig. Take out the detector vertically to avoid any damage to the mirror inside the chamber and the KRS crystal on the detector.
3) Screw the vacuum adapter carefully on the back of the detector and carefully take out the o-rings.
4) Put Krytox grease on all o-rings and fittings to clean and grease it.
5) Connect the pump tube to the turbo pump.
6) Put the vacuum adapter back on the detector by carefully screwing it to the groove and put the nut and tighten it with fingers (additional tightening is not required) on top and pull the shaft to the open position.

Section 4: Waste Disposal/Cleanup

Dispose of liquid waste accordingly.

Section 5: Emergency Response

Power is lost

- Close CO/He tank (next to Vertex), O_2 tank (near next to Vertex), and SF_6/He and H_2 tanks (next to Direct synthesis hood) – pure CO tank will be closed by gas cabinet automatically with loss of power
- Turn off power switch on Vertex FTIR, Legato syringe pump, and mass spectrometer
- Turn off power switch on variac and Watlow controllers
- Call F&S

CO Alarm

- Inform everyone to move to safety
- Close bellows valve on MFC Manifold
- Close hood completely
- Press red “Shutdown” button on gas cabinet (if flowing pure CO)
- Move to safety

Gas Cabinet Alarm for CO

- Close bellows valve on MFC Manifold
- Press red “Shutdown” button on gas cabinet for CO

This happens when gas is flowing too fast out of the gas cabinet, which ***could*** indicate a leak. It can also occur if a vacuum pump is pulling directly on the CO tank on the Tensor system. If the cause is known and not a leak into the room, shutdown the flow (steps above) and silence the alarm. If the cause is unknown, shutdown the flow (steps above) and inform everyone to move to safety.

Water leak above

- Turn off power strip that switches and unplug Vertex FTIR, computer, Legato syringe pump, Alicat MFCs (only unplug), Watlow controllers, Series Pump, and variac
- Cover FTIR (particularly detector on left side and the right back corner where the beam splitter sits) as best as possible with catch pans
- Cover Alicat MFCs with absorbent pads
- Move smaller electronics to safe, dry space
- Call F&S

Fire

- Inform everyone to move to safety
- Call 911
- Follow fire safety procedures using fire extinguisher if possible or exit to safety
- Only as long as you feel safe, turn off main valves for…
    - CO/He, and O_2 tank in fume hood
    - SF_6/He and H_2 tanks near direct synthesis hood
    - CO tank in gas cabinet

Checklist:

☐ Read (Material) Safety Data Sheets.

☐ Proper fire extinguisher is nearby.

☐ Another researcher is nearby and knows the hazards present.

☐ All potential peaks are known prior to beginning the procedure.

☐ CO detector batteries are good

☐ Gas tanks are open

☐ Detector cooled

☐ Crystal polished and transmission measured prior to coating with catalyst

☐ Sample has a signal 13,000-30,000 and peak position at 59426

☐ Leak check

☐ Thermocouple attached

☐ Heating cartridges are fully inserted into heating block and grounded to ATR cell

☐ Change file name and path

☐ Background scan

References:

OPUS to CSV Macro: Z:\DWF Group\MEW Research\FTIR\OPUS_TO_CSV_BY_FOLDER.mtx

Directions for Alicat MFCs: Z:\DWF Group\Wiki\Safety\SOPs\Using Alicat MFCs on FTIR_20171118.docx

Watlow User Manual: Z:\DWF Group\Wiki\Manuals\WATLOW.pdf

OPUS, Vertex, and Alicat user manuals found in drawer under Tensor.

Training Documentation

Signing this document means that you have read and understand all aspects of this Standard Operating Procedure. The supervisor is the person that acknowledges you took the training and understand the procedure. They can be a lab manager or researcher assigned by the PI to oversee this particular SOP.

Name (Printed)	Name (Signed)	Supervisor	Date