Gas Transmission FTIR

Standard Operating Procedure

Lab: Davenport 270

Department: Chemical and Biomolecular Engineering

PI/Manager of Space: Prof. David Flaherty

Written By: Megan Witzke Revised By: Zeynep Ayla, Chris Torres

Section 1: Overview

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

Synopsis:

This SOP is to provide guidelines and standard procedures for the Gas Transmission FTIR. This technique can be performed on both the Bruker Tensor and Bruker Vertex instrument.

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
Carbon Monoxide	Toxic, flammable, asphyxiant
Hydrogen	Flammable, asphyxiant
Helium	Asphyxiant
Carbon dioxide	Asphyxiant
Oxygen	Flammable

Relevant References for Material Hazards:

Carbon Monoxide
https://airgas.com/msds/001014.pdf

Hydrogen
http://airgas.com/msds/001026.pdf

Oxygen
http://airgas.com/msds/001043.pdf

Carbon dioxide
https://www.airgas.com/msds/001013.pdf

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

Equipment Hazards:

Watlow controller and heating cartridges—electric shock, high current, high temperature

Mechanical pumps—electrical shock

Legato syringe pump—electrical shock

Variac and heating tape—high temperature, electric shock

Syringe needles—sharps hazard

Hazardous Conditions:

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. Turn on roughing pump to be able to evacuate lines in case of emergency. Do not use line with rubber septum while using CO. Pressure check the cell and insure leak rate is < 0.25 psi/ 5 min at 6 psi.

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

Technique Hazards:

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.

Engineering Controls

CO and H_2 are 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 and heating cartridges are pumped 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.

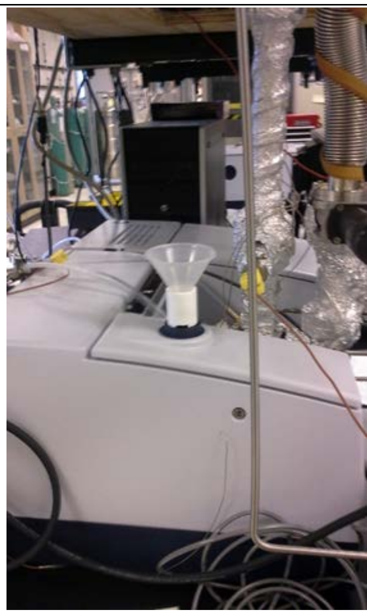
CO detector should be kept near FTIR system (on shelf, near temperature controllers). Check batteries prior to flowing CO. Turn on roughing pump in mechanical room prior to flowing CO to evacuate manifold in emergency.

Exit gases are piped directly into exhaust system.

Section 3: Procedures

Start-up Procedure

1. Turn FTIR power on via a power switch at the rear of the system, directly above the power connection. Upon powering up wait about 5 minutes for the system to become fully operational.
2. Open OPUS 7.0, the software used to take measurements via the Bruker TENSOR 37 FTIR. PW: OPUS



Liquid nitrogen funnel inserted into dewar on Tensor 37 FTIR

3. Insert the liquid nitrogen funnel into the detector dewar as shown in above. Fill MCT detector slowly with liquid nitrogen until the funnel is full. Allow time for the funnel to drain into the dewar and repeat. It is very important to not overfill the dewar. This can cause irreparable damage to the detector. To prevent this issue always watch the blue plastic spacer ring that the funnel sits on. When the dewar begins to approach capacity, liquid nitrogen will start splashing into this spacer ring. When this occurs the filling is complete and one should dump any remaining liquid nitrogen in the funnel and place the dewar cap on the plastic spacer.
4. Cooling can be confirmed on the instrument (indicator in the top right-hand corner should be green, not red) and through the OPUS software. On the top toolbar select Measure>Advanced Measurement. Navigate to the check signal bar and wait a moment for the FTIR to scan. The intensity should read between 10,000 and 30,000 if the correct amount of sample has been loaded, the optics are properly adjusted, and the detector is cooled. The peak position should be between 58000 and 62000, significant deviation from this range (or a wandering peak) may be indicative of problems with the IR laser. The standard optics settings used are 4x gain and 6mm aperture size, though this can be adjusted to optimize signal.

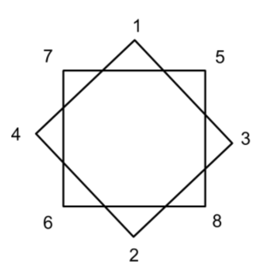
Making an IR pellet

1. Grind 25-50 mg (or desired amount) of dry catalyst powder in a mortar and pestle for at least 3-5 minutes. The purpose of grinding is to obtain a very fine catalyst powder. (< 200 mesh)
2. Fully clean and dry a pellet press mold. The pellet mold is comprised of two 20.34 mm diameter stainless steel cylinders (heights of 32.42 mm and 15.97 mm) and a rectangular stainless steel casting (63.5 mm x 38.18 mm x 50.05 mm) with a 20.39 mm cylindrical orifice centered on the shortest side to serve as the structural support for the cylinders. The two cylinders have a letter (T or B) stamped into one side and the other side has a knife edge. The two knife edges should face each other when the mold is fully assembled. Two separate stainless steel squares sandwich the mold on top and bottom when fully assembled to create flat surfaces when in the pellet press.
3. Place a piece of weigh paper on one of the steel squares. Place the support structure on top of the weigh paper. Place the longer of the two cylinders is placed into the support structure with the knife edge facing up.
4. Slowly begin pouring the catalyst into the mold. It is extremely important that the powder is uniformly spread over the surface, because once this step is completed, it is difficult to change the uniformity of the sample. Uniform spreading can be achieved by creating a slight mound in the center of the mold and then slowly twirling a spatula through it.
5. It is very important to further distribute the sample uniformly without leaving any discrete lines within the distributed sample by tapping the side of the mold with a wrench to create small vibrations to help the sample distribute well. By the end of this step, you should have what appears like a single piece distributed uniformly and without any discrete lines in it.
6. *Slowly* place the other cylinder atop the ground catalyst with the knife edge facing down. The mold is a pretty tight fit. If you move it too fast, the air rushed out will blow the sample powder around. Gently turn the top cylinder to ensure the catalyst is still uniformly distributed.
7. Transfer this entire stack onto the Carver Hydraulic Laboratory Press. Slip in the second stainless steel square on top of the pellet mold and carefully hold while applying force with the hydraulic press.
8. Apply a pressure of 5000 psig to the assembly for 60 seconds. Increased the pressure to 10,000 psig for an additional 60 seconds.
9. Release the pressure of the press. Make sure to hold the top steel square so it doesn't fall off of the pellet mold. Remove the mold from the press.
10. Slowly remove the top cylinder from the mold while rotating.
11. Carefully slide the mold off the steel square and support the bottom cylinder with your finger.
12. Gently push the bottom cylinder up through the support structure so you have access to the pellet directly.
13. Remove the sample pellet with the cylinder top carefully by pushing the pellet with a spatula onto a piece of weighing paper. This takes some practice and patience.
14. Measure the total weight of the sample pellet.

Loading the cell

1. Clean the Transmission Flow Cell with the acetone sprayed onto a Kimwipe to remove any remnants of the previous user. The graphite ferrule remaining in the cell will come off black/gray—don't worry about this.
2. **Clean your CaF_2 windows with acetone and a Q-tip—a Kimwipe will leave tiny scratches and reduce the transmission**.
3. Lay the cell with the thermocouple tip facing up towards you—not the counter. There should be a flat steel ring to lay the sample holders on. I recommend placing a Kimwipe and weigh paper under the cell in case the pellet breaks during the loading process.
4. Insert the bottom sample holder into the cell aligning the thermocouple tip with the notch, and the recessed part facing up. (CAD drawings are useful here)

5. Carefully place the catalyst pellet using the weigh paper onto the sample holder. Adjust the pellet so it sits just inside the recessed part of the holder. It should be a pretty good fit.
6. Using tweezers, lower the top of the sample holder onto the catalyst pellet. Align the notch with the thermocouple. Careful not to drop the top of the sample holder, otherwise you risk breaking the pellet.
7. Place the sample holder retainer ring (see CAD drawings) carefully on top of the sample holders without cracking the sample pellet. Works best to slightly push the ring into the side of the cell while sliding it down. Watch your glove so it doesn't poke the pellet.
8. Gently place the CaF_2 window (see CAD drawings) in the center of the IR cell and on top of the sample holders. Again you don't want to break the pellet.
9. Place the custom designed graphite ferrule (30.0mm OD, 25.6mm ID, overall length 6.0mm, Bevel length 4.2mm) around the CaF_2 window, and push it up against the sample holder retainer ring with the ferrule backer (see CAD drawings). Push the ferrule in while keeping the ferrule backer level with the table. This is important so pressure is evenly distributed around the window to avoid cracking the window.
10. Finger-tighten the 8 screw set.
11. Place the window retainer (see CAD drawings) on top of CaF_2 window and barely finger tighten the 2 screws.
12. Flip the cell over.
13. The graphite ferrule is typically left in place on this side and is fine to reuse many times.
14. If there is no graphite ferrule in place, insert the CaF_2 window then add the ferrule as you did in step 9. If the graphite ferrule IS still in place, insert the CaF_2 window, however now you will need to push the window so it sits fully recessed and below the level of the outside of the cell—this is done by pushing straight down on the window with 2 thumbs. It is important to make sure that the window is fully recessed otherwise the ferrule backer and window retainer will crack the window.
15. Finger-tighten the 8 screw set.
16. Place the window retainer (see CAD drawings) on top of CaF_2 window and barely finger tighten the 2 screws.
17. Check the transmission of the pellet by placing the cell into the insulating box/heating setup. On the top toolbar select Measure>Advanced Measurement. Navigate to the check signal bar and wait a moment for the FTIR to scan. The intensity should read between 12,000 and 30,000 if the correct amount of sample has been loaded, the optics are properly adjusted, and the detector is cooled. The standard optics settings used are 4x gain and 6mm aperture size. The gain can easily be changed to be within the proper transmission region.
18. Remove the cell from the heating setup.
19. Methodically tightening the 8 screw sets in a star pattern using the torque wrench set to 20 lb in. The star pattern is shown below:



Do one side of the cell at a time. Start by tightening a half turn through all 8 on one side. Next a quarter turn through all 8. Next an 1/8 turn. If at any point in time the torque wrench 'breaks,' that is your indicator to stop and move to the next screw. At this point, you will be close to done and just go through the star pattern once more so that the torque wrench 'breaks' at each screw. You can always tighten more, but you can't uncrack your window.

20. Repeat on the other 8 screw set.
21. **Do not tighten the window retainers with anything other than your fingers!**
22. Place the cell back into the insulating box/heating setup. The cell should face in such a way that the 1/8" and ¼" female nuts can be connected to the appropriately sized unions on the cell. Double check the transmission again.
23. Pressure check the cell by closing the ball valve downstream of the cell and flowing 10 sccm of He until a pressure of ~6 psig builds up. Stop the flow on the MFC and check that leak rate is < 0.25 psig / 5 min. Release the pressure by opening up the ball valve downstream of the cell. If liquid injection port will be used during experiments, cap the injection port for the pressure check, but replace it before pretreating the catalyst. If liquids will not be used, remove the injection port lines and replace with 1/8" line to avoid contamination. *Directions on how to use the MFCs can be found in the document 'Using Alicat MFCs on FTIR_20171118.'*
24. Slip the cell thermocouple lead through the hole in center of the top aluminum heating block and fasten the top block to the bottom block. You just need to finger-tighten these screws. Make sure the holes for the heating cartridge are facing the front (towards you). Double check the transmission.
25. Insert the heating cartridges into the heating block completely. If these are not fully inserted, they will disproportionally heat and glow red/orange. Ground the heating cartridges to the insulating box.
26. Slip the cell thermocouple lead through center hole in the top of the insulating box.
27. Find the heating block thermocouple with the ceramic holder and slip that through the side hole in the top of the insulating box. The tip of this thermocouple needs to sit just inside small hole the aluminum heating block. Keep the heating block thermocouple in place while snuggly fitting the top of the insulation box onto the bottom of the box. A better fit of the box with the thermocouple in place will help the heating process (i.e., keep it more stable, decrease the offset in temperatures between the cell and heating block thermocouples).
28. Add the yellow thermocouple connection to leads of the cell thermocouple. Yellow is positive, red is negative.
29. Plug the cell thermocouple into the Watlow controller marked 'Reactor', turn on the controller, and check that the temperature makes sense (~25ºC). Leave this Watlow controller on throughout the entire experiment—it doesn't control anything but is important to inform others if the cell is hot or not.
30. If needed, wrap the transfer lines with heat tape and insulation. Plug the heat tape into the power strip leading to the variac. Turn on the variac and set to the appropriate output voltage. You'll need to figure out what that is for your particular reactant, but 2-3 works well for keeping something ~50ºC. Overheating may cause inconsistent liquid flow. Under heating may cause pooling in the lines. In general, you don't want to use too high of vapor pressures, because the lines all the way up through the exhaust are not heated.

<u>Pretreating the catalyst</u>

1. Begin flow of the desired gas composition.
2. Turn on the Watlow controller connected to the heating block thermocouple.
3. Change the setpoint directly on the Watlow controller or using EZ-Zone program (the controller will need to be connected to the computer with the DB-9 to USB cable). Use EZ-Zone to check any other parameters you want to customize (e.g., ramp rate, PID values)
4. Turn on the switch for the output on the Watlow controller.
5. **Stay near the setup and watch the temperature** on the controlling Watlow. It will take some time (1-2 min) to respond to the output of the heating cartridge. Make sure the temperature responds in the cell as

well. This will take even longer to respond because the conduction into the cell takes some time. I recommend heating in increments to your setpoint—heat to 50ºC, wait for the cell to catch up, heat to 100ºC, wait for the cell to catch up, … slowly approach your desired setpoint so you don't over shoot significantly. This slows the process down and allows you to catch mistakes earlier. There will be some offset in temperatures between the cell and the heating block depending on the placement of the heating block thermocouple, so give the temperature plenty of time to settle.

6. If needed, a small fan can be used to cool the setup faster after completing the pretreatment.

Running experiments

1. Setup the file name and destination using OPUS. Measure> Repeated Measurements. Complete the sample description including catalyst name and pretreatment conditions. Save to the local computer during experiments.
2. Once the temperature for experiments is reached, check the transmission signal intensity again and adjust gain as needed.
3. Choose the number of scans per measurement and resolution that work best for your experiment (balance signal to noise vs. time resolution). CaF_2 windows only transmit to ~1300 cm^{-1}. KBr windows transmit significantly lower ~400 cm^{-1} but are weak and dissolve in water. Taking wider wavenumber ranges doesn't affect the time resolution, but you'll be collecting useless data points.
4. Take a background scan under appropriate gas composition (Measure>Repeated Measurements).
5. During experiments, keep track of temperature—drifting temperatures can drastically affect the baseline.
6. **If liquid injection port is being used:** Control liquid flow rates using the Legato syringe pump.
    a. Select the syringe (Manufacturer and Size)—most common brands and sizes are listed. If not create a custom syringe with accurate inner diameter of the barrel.
    b. Specify flow rate and length of time or total volume to inject. Check your units.
    c. Fill your syringe, make sure there are no bubbles.
    d. Place syringe on Legato pump by securing the syringe barrel and the barrel flange appropriately.
    e. Push the pump carriage to the end of the plunger and squirt out just a drop of liquid to make sure the needle is filled.
    f. Start scanning before inserting the needle into the rubber septum.
    g. Carefully insert the needle through the rubber septum and as far in as possible so the end of the needle will sit in the cross flow of the gas.
    h. Select 'Run' on the pump.
7. A bubbler/saturator can also be used in line with the gas flow while sitting in an ice water/dry ice and acetone bath. This is useful for volatile liquids such as acetaldehyde that would boil at room temperature.
8. Refill the liquid N_2 detector as needed. It should last ~6-8 hours. The baseline will start creeping up as the detector starts warming—you want to avoid this.

Ending experiments

1. 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.
2. Stop liquid flow on Legato pump. Remove the syringe from the rubber septum.

3. Stop gas flow on MFCs. Flow 5 sccm of He and close other bellows valves for gases. If using toxic gases, allow significant time to flush lines completely before loosening any gas fittings.
4. Turn off Watlow controller for cartridge heaters.
5. Wearing thermal insulating gloves, lift off insulating box. Use small fan to cool cell.
6. Turn off variac, unplug heat tape, and unwrap transfer lines.
7. Once cell is cooled, remove cell thermocouple from Watlow controller and take of the yellow thermocouple connector.
8. Take of insulating box, and aluminum heating block. Careful not to tangle or pull on the cartridge heaters.
9. Remove cell from setup by loosening the gas fittings on either side of the cell.
10. Unload the cell by loosening the screws in the reverse methodical fashion as you tightened them (small turns first in the star pattern, then slightly larger turns, … . You can use the torque wrench here, or the 9/64” Allen wrench. Use the nice allen wrench from the UHV set to keep the screws in the best condition. **Put the allen wrench back after using it.**
11. The window retainer and ferrule backer will come off after the screws are removed. The windows will have a tight seal with the graphite and need to “pop out”. Finger tighten a ¼” cap on the ¼” union. Place both hands (wearing nitrile gloves) over the windows (one on each side). Blow compressed house air into the 1/8” union while cupping your hands around to catch the windows as they pop out.
12. It is possible that only a single window pops out. That’s ok. Push the other window out onto a Kimwipe using your thumb.
13. If the sample holders don’t get pushed out with the second window, push those out with your thumbs. These can only come out the same direction that they went in.
14. If roughing pump is on (from using CO), turn it off using the switch in the pump room.
15. Clean up the area. Syringes emptied, needles protected in a rubber stopper, tools put away, cell stored in proper IR drawer (all of the parts including the graphite ferrule). Store your windows away.

Section 4: Waste Disposal/Cleanup

Destroyed catalyst pellets should be disposed of in solid waste if compatible.

Section 5: Emergency Response

Power is lost

- Close CO_2 tank (next to Tensor), O_2 tank (near UHV), and He tank (in gas cabinet) – CO and H_2 tanks will be closed by gas cabinet automatically with loss of power
- Turn off power switch on Tensor FTIR and Legato syringe pump
- Turn off power switch on variac andWatlow controllers
- Call F&S
- Call Tomas/Chris

CO Alarm

- Inform everyone to move to safety
- Open roughing pump bellows valve
- Press red “Shutdown” button on gas cabinet
- Move to safety
- Call Tomas

Gas Cabinet Alarm for CO

- Open roughing pump bellows valve
- 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. 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.

Gas Cabinet Alarm for H_2
- Press red "Shutdown" button on gas cabinet for H_2
- Close bellows valves H_2

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 H_2 tank. If the cause is known and is 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 switches and unplug Tensor FTIR, computer, Legato syringe pump, Alicat MFCs (only unplug), Watlow controllers, and variac
- Cover FTIR (particularly detector on left side near pump room) as best as possible with catch pans
- Cover Alicat MFCs with absorbent pads
- Move smaller electronics to safe, dry space
- Call F&S
- Call Chris/Tomas

Fire
- Inform everyone to move to safety
- Call 911
- Follow fire safety procedures using fire extinguisher if possible or exit to safety
- Call Chris/Tomas
- Only as long as you feel safe, turn off main valves for…
    - CO, H_2, and He tanks in gas cabinet
    - CO_2 tank next to Tensor
    - O_2 tank near UHV

Section 6: Additional Information

Advice:

Keep detailed notes on the scans—temperature, pressure, flow rates.

Before beginning experiments, write down where you expect to see peaks, and what vibrations the peaks indicate. Note any 'mystery' peaks. Are they from water? CO_2? Hydrocarbons? Are they growing/shrinking with time?

Use your right hand when checking electrical connectivity. If you've mistakenly left the power on, using your right hand will avoid putting your heart in a circuit if you get shocked.

Oil in mechanical pumps should be changed monthly.

Purge gas generator (Parker) is shared with Vertex FTIR. If CO_2 and water peaks are growing/shrinking, check that the Vertex sample compartment is closed and that the connections on the lines purge gas lines are tight.

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
☐ Pumps are turned on and oil levels are appropriate [for CO use]
☐ Gas tanks are open
☐ Check with UHV system prior to using O_2
☐ Sample has a signal 12,000-30,000
☐ Leak check
☐ Thermocouple polarity is correct
☐ Heating cartridges are fully inserted into heating block and grounded to insulating box
☐ Thermocouple for heating block is inserted
☐ 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

CAD design, and previous literature for gas transmission cell: Z:\DWF Group\In Situ FTIR Cell\Description of Use and Paper of Use in WGS

OPUS, Tensor, 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