FOURIER TRANSFORM INFRARED SPECTROSCOPY

Purpose and Scope:

This document describes the procedures and policies for using the **MSE Bruker FTIR Spectrometer.** The scope of this document is to establish user procedures. Instrument maintenance and repair are outside the scope of this document.

Responsibilities:

This document is maintained by the department Lab manager. The Lab Manager is responsible for general maintenance and for arranging repair when necessary. If you feel that the instrument is in need of repair or is not operating correctly, please notify the Lab Manager immediately. The Lab Manger will operate the instruments according to the procedures set down in this document and will provide instruction and training to users within the department. Users are responsible for using the instrument described according to these procedures. These procedures assume that the user has had at least one training session.

Warnings and precautions:

- When using the EGA-TGA Cell remember that it is hot. The cell and the line from the TGA to the cell are operated at 200C.
- When using the EGA-TGA cell please remember to turn off the heater by pressing the down arrow on the controller until the set point reads "off". You will be shown how to do this during training.
- User are NOT cleared to change out fixtures. Only lab personnel are allowed to install or remove the ATR, the pellet holder, the EGA-TGA Cell or any other fixtures. We recommend that you notify lab personnel the day before your scheduled measurement to ensure it is ready.
- For measuring KBr pellets: Users are expected to make/have their own pellet equipment. This includes the punch and die, the KBr, mortar and pestle, and any other equipment you deem necessary.
- Do not attempt to "fix" or adjust or calibrate any part of the instrument or software. If you need a different configuration, please notify lab personnel of your specific needs and we will make every attempt to accommodate you.

Background

From MSE 313 FTIR Lab Manual

Fourier Transform Infrared Spectroscopy (FTIR) is an important technique that provides an easy way to identify the presence of certain functional groups in an organic molecule. Functional groups have vibration frequencies that are characteristic of that functional group. These vibration frequencies fall with the infrared (IR) frequency range. As such, passing an IR signal through the organic compound causes the functional groups to vibrate at specific frequencies. In other words, an infrared signal that passes through an organic compound will be absorbed at these characteristic frequencies, which can be transformed into a unique spectrum.

Figure 1 below shows the instrument in the Mueller lab. Figure 2 is a schematic of the Bruker Vertex 70. The beam from an IR source passes through a monochromatic controller with a selector, ensuring that only specified wavelengths are emitted, which may vary from 4000 to 400 cm^{-1}. The sample is placed in a holder in the path of the IR source. A detector reads the analog signal and converts the signal to a spectrum. A computer is used to analyze the signals and identify the peaks.

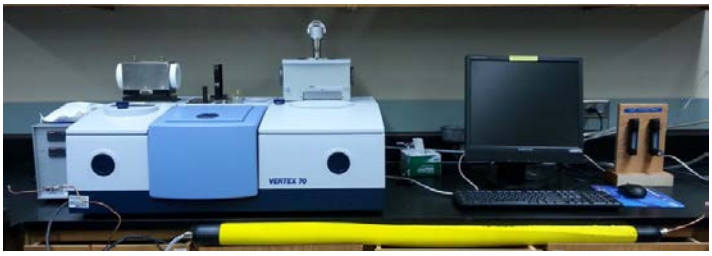


Figure 1 - MSE FTIR in Mueller 170

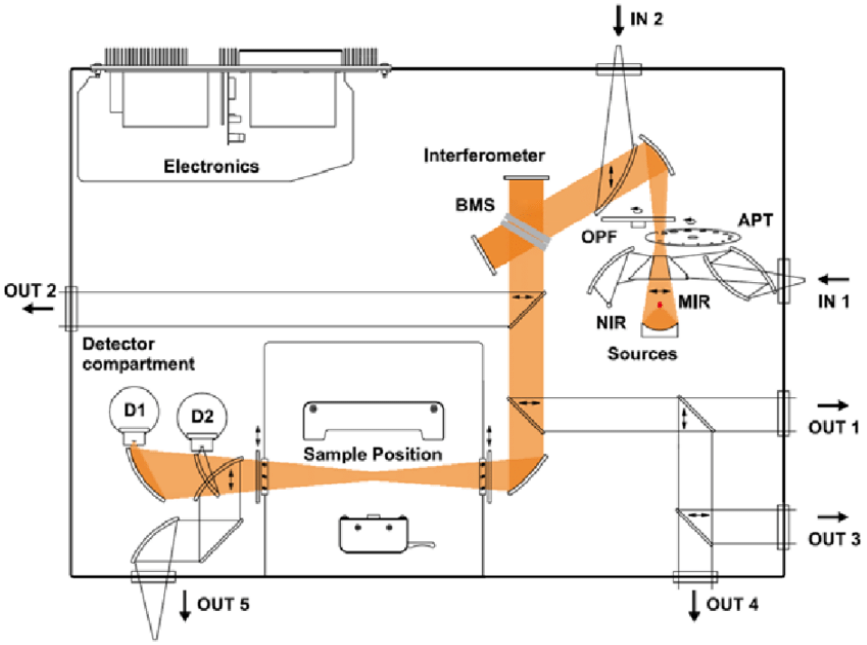


Figure 2 – schematic of the Bruker Vertex 70 (Bruker.com)

An IR beam goes through a partially silvered mirror, which splits the beam into two beams of equal intensity. One portion of the beam goes through the sample. The other is guided through the machine with mirrors. The sample will absorb some of the energy of the IR source depending on the functional groups that are present. A wave pattern is created from the constructive and destructive interference that occurs when the two beams meet. This resulting wave is known as an interferogram, which looks nothing like a spectrum.

Fourier transform changes the data from intensity as a function of time into intensity as a function of frequency (more commonly wavenumber) to reveal an IR spectrum. The IR spectrum can be presented either as absorbance or transmission. The absorption is typically presented as downward peaks in an IR spectrum (cf. UV-vis spectroscopy where absorption is an upward peak).

Carbon dioxide and water are always found in the spectra. Carbon dioxide is seen as the doublet at approximately 2400 cm^{-1}. Water is seen at 3800 and 1600 cm^{-1}. FTIR machines have systems to purge the atmosphere (replace the existing atmosphere with a gas) every time a new sample is analyzed; however, because of the atmospheric variations, a background spectrum is required about every 30 minutes and every time a new set of parameters are entered. Samples can be mixed with KBr or NaCl and prepared as a pellet because those materials are invisible to infrared. KBr and NaCl pellets are very fragile and have to be handled with care.

Some spectrometers come with an attachment know as an ATR (attenuated total reflection) which does not require pellets. ATR is a reflection technique where the IR beam is directed through an internal reflection element (IRE) with a high index of refraction. The IR light is totally reflected internally off the back surface, which is in contact with the sample. The sample must have a lower index of refraction than the IRE to achieve total internal reflection. Upon reflection at the IRE/sample interface, the IR light penetrates into the sample to a small degree and the IR data from the sample are obtained.
For more information about FTIR spectroscopy please refer to the Bruker tutorial in the OPUS software provided.

Users are given a dvd with the OPUS software to download on their lab computers. (requires Win. 7). ***Please download the software before your second training session. This software contains an interactive FTIR tutorial in the help menu and users are strongly encouraged to complete the tutorial before their first measurement***

Procedure

There are a number of different configurations available. We have a diamond ATR, a pellet holder, an 85-degree reflectance module and a EGA-FTIR cell for measuring decomposition gases from TGA. Each configuration is discussed but some basics are the same.

Basics:

- First verify that the instrument is on (it should never be turned off). And that the N2 is flowing properly. There should be between 3 and 5 SCFH. Do not make changes to the tank pressure. If you think it needs to be changed, please contact the Lab Manger/Assistant.

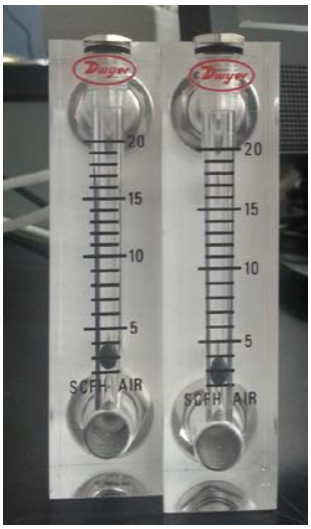


Fig. 2 Chamber and sample purge flow meters

- Open the OPUS software and sign in:

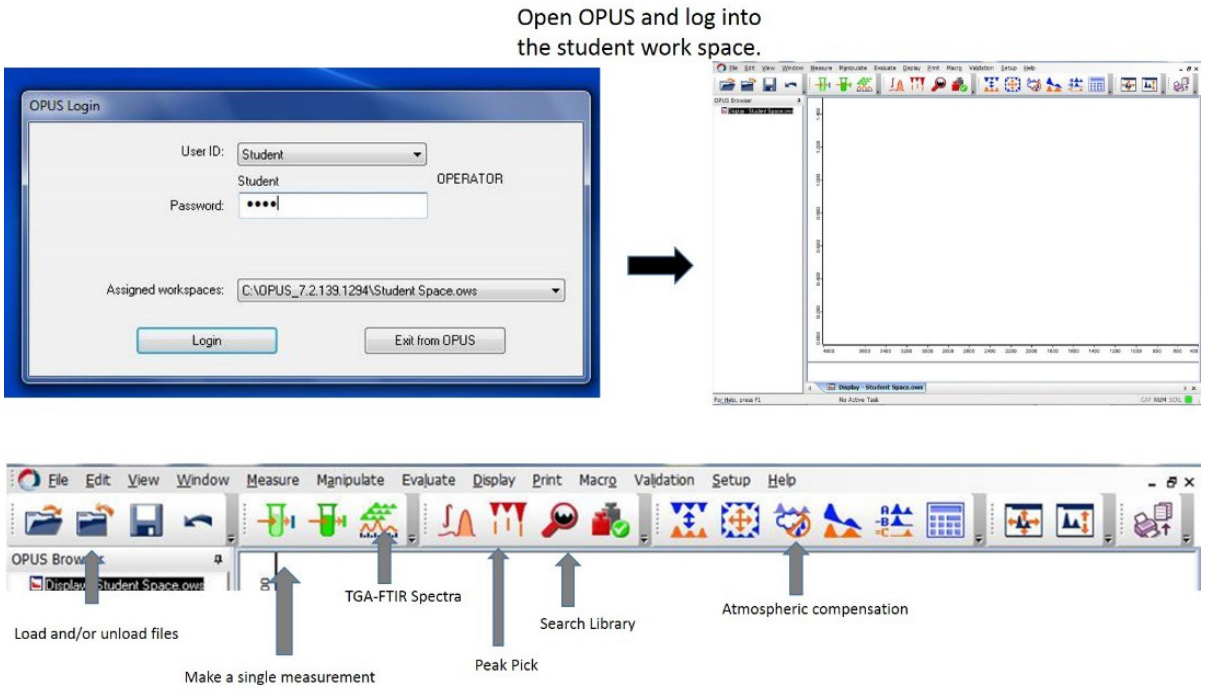


Fig. 3 Log in and work space

Using the ATR

Fig. 4 ATR

- Do not attempt to install the ATR. Contact lab personnel if necessary.
- Using a Kim-wipe and IPA, wipe down the surface. (Never pour IPA directly on the surface)
- Never use any other solvent.
- Under the 'Measure' menu select 'cleanliness test'.
- If the test returns a value of 2.0 or higher please contact the lab manager.
- If value is below 2.0 you are ready to proceed. You will want to open up an experiment file that contains all of the measurement parameters. (This is usually created for you during your training session). Select the "single measurement" icon.
- There are three main tabs you will use to define and save your measurement: "Basic", "Advanced", and "Check Signal"

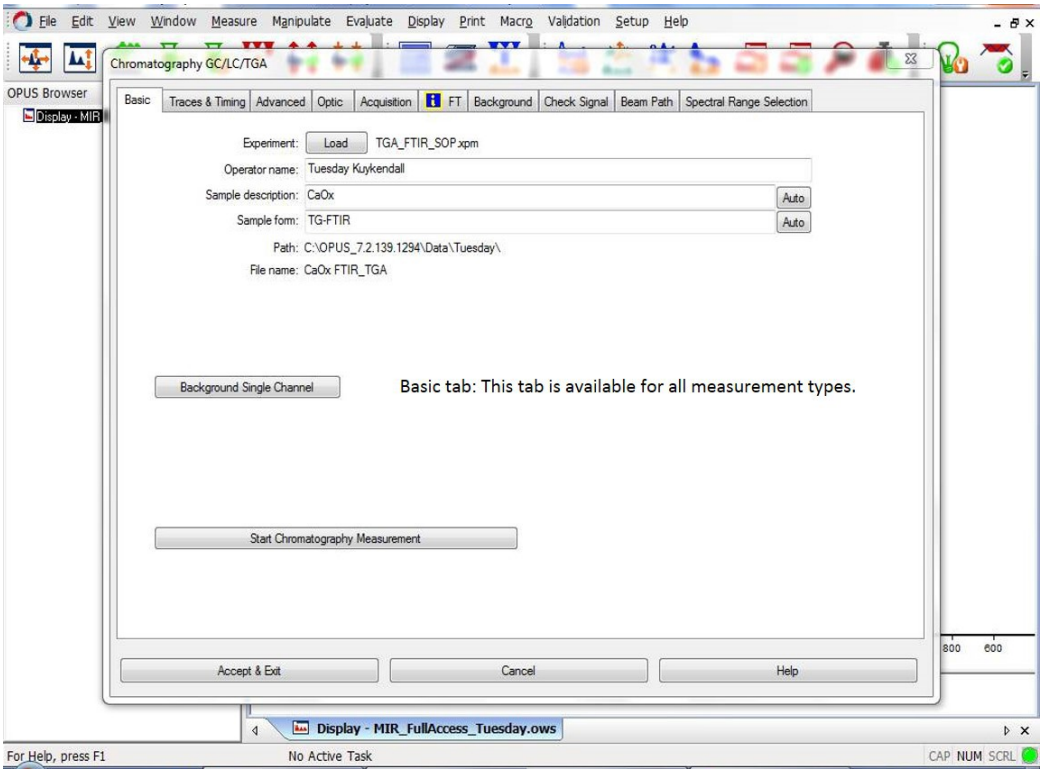


Fig. 5 Basic Tab

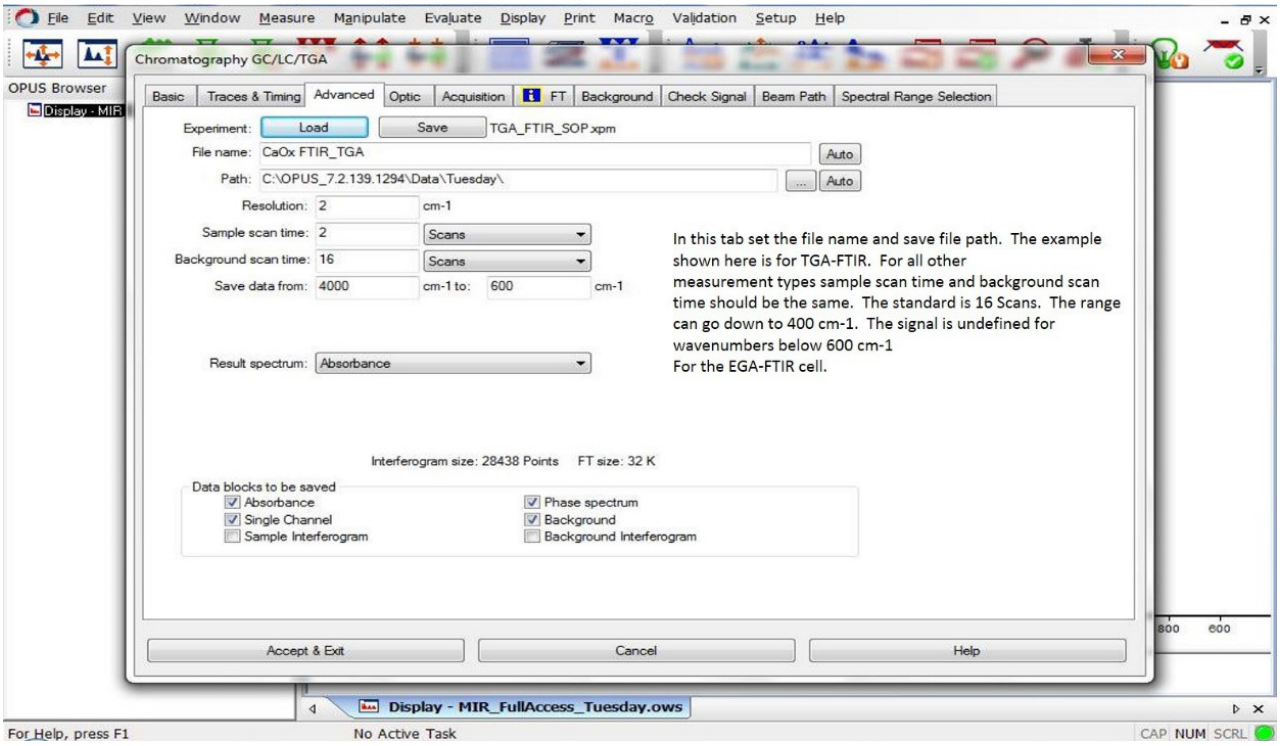


Fig. 6 Advanced Tab (Chromatography)

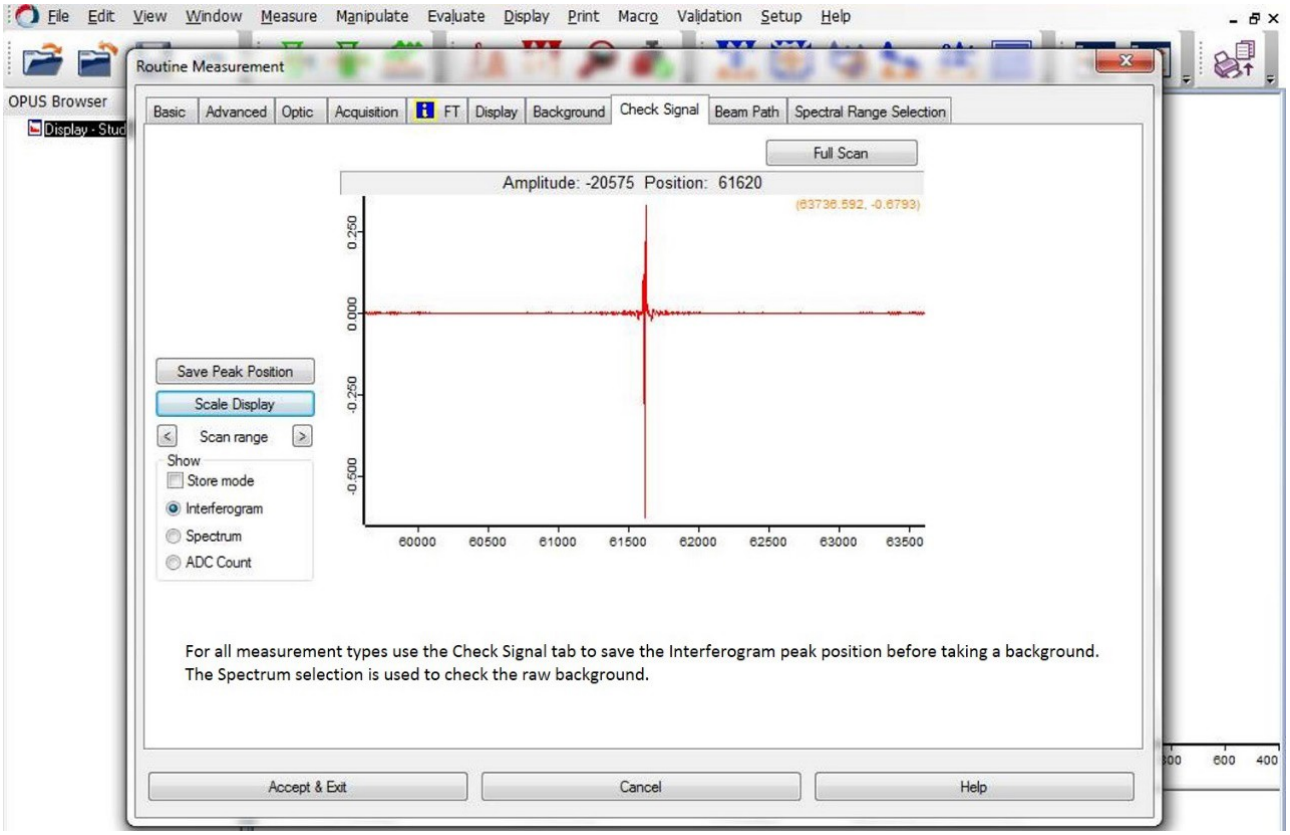


Fig. 7 Check Signal Tab

- Load your pre-defined experiment file from the basic tab. You can save your data file and define the file path in

the Advanced tab. This is also where you can make changes to your parameters. For example, under result spectrum you can choose Absorbance (default), Transmission, Reflection, etc. The maximum wavenumber range is from 400 cm-1 to 4500 cm-1. (For the EGA-cell signal below 600 cm-1 is undefined).

- Next select the "Check Signal" tab. Before running a background, the chamber should be purged to eliminate the CO2 peak as much as possible.

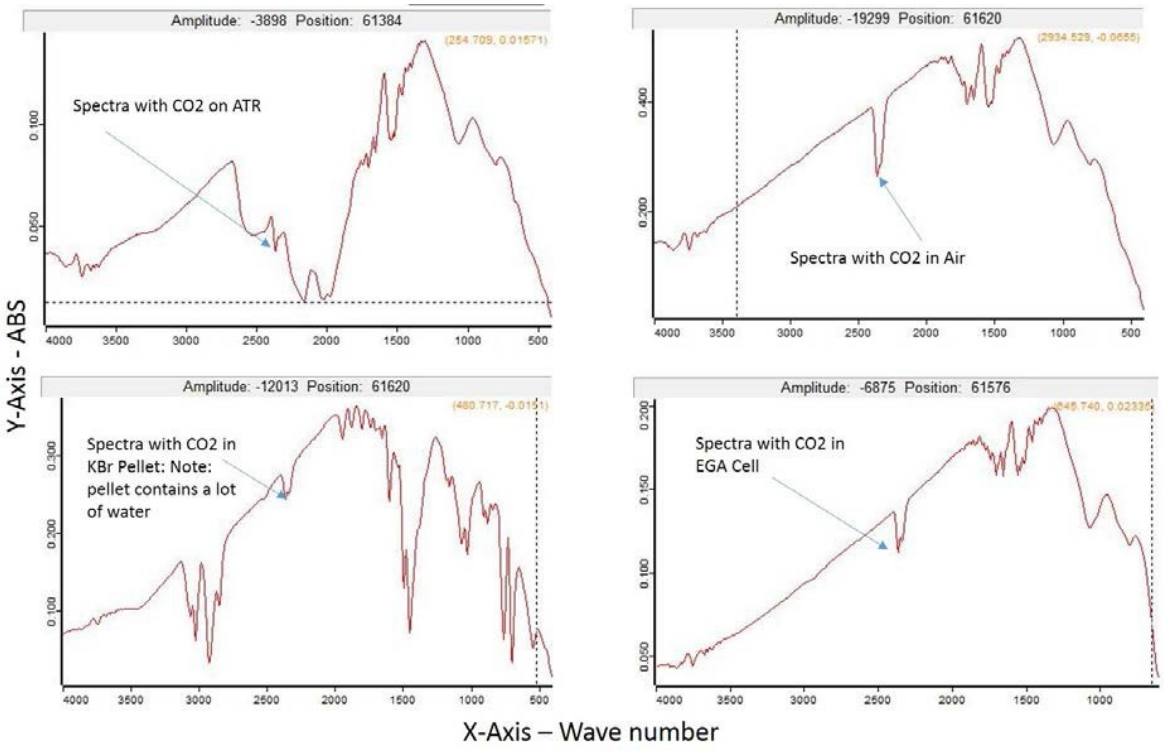


Fig. 8: Examples of Scans with CO2 peak – before purge

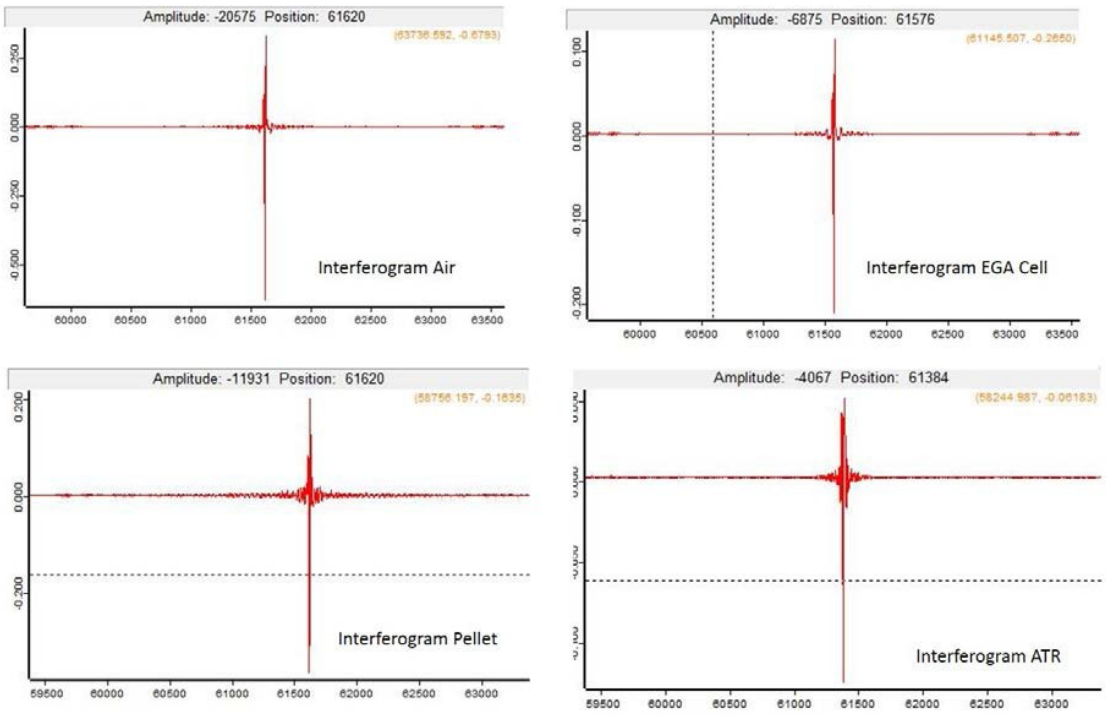


Fig. 9 Various Interferograms. Note the different amplitudes.

- When purge is complete, select the Interferogram and then select "Save Peak Position". This must be done BEFORE a background is taken. A background is required before each measurement.

- Note that the ATR background is attenuated between 2000 cm-1 and 2500 cm-1. This is due to the diamond platform and cannot be eliminated.

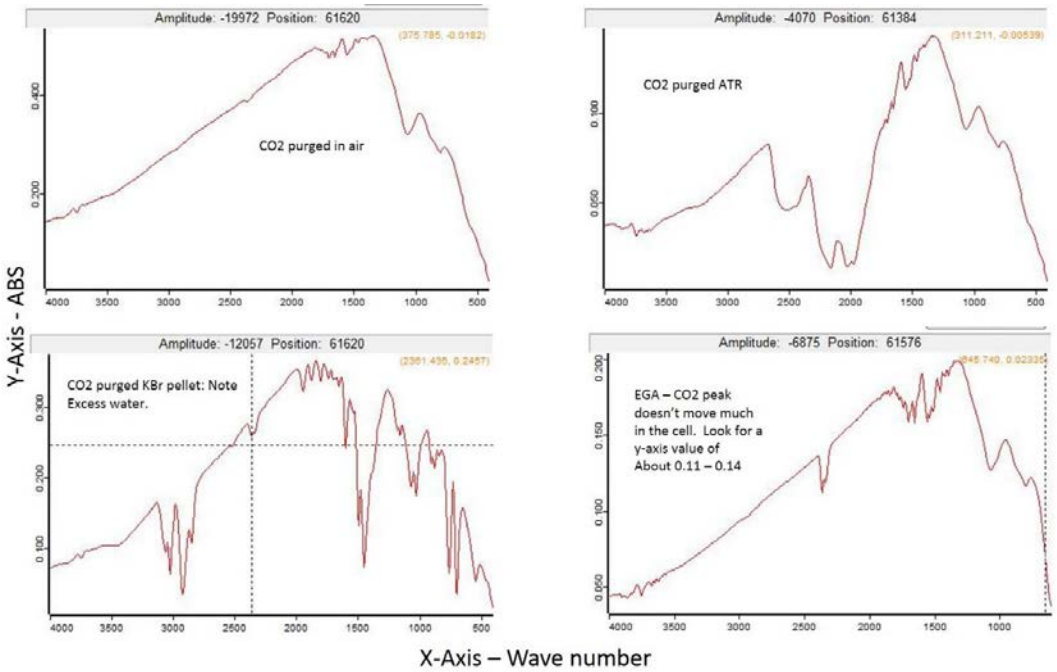


Fig. 9: Purged background spectra

- From the basic tab, run the background. The bottom of the screen will indicate when the background scans are complete.
- Place your sample over the diamond stage and press down the pressure clamp. The red centering dot should show in the middle of the clamp indicator.

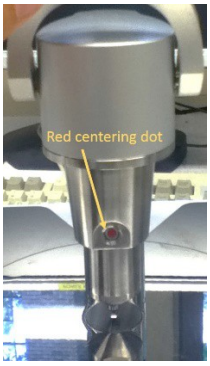


Fig. 10 Pressure clamp red dot

- If you are measuring a liquid (CHECK WITH LAB MANAGER FIRST!) then pour the liquid over the diamond platform and place the cover provided over it. – Be sure to move the pressure applicator out of the way.

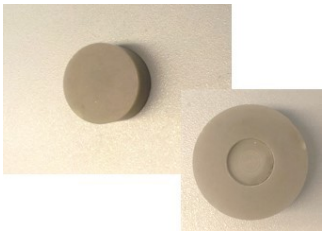


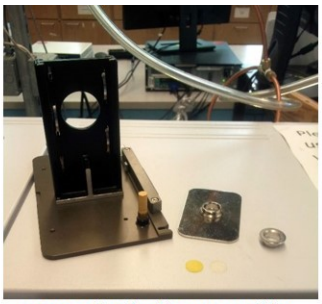
Fig. 11 liquid cover

- In the basic tab select Single Channel Measurement. The bottom of the screen again indicates when the scans are complete.
- Remove your sample and clean the diamond stage.
- If you are finished you may save your data onto a USB drive. If you need to run another sample repeat the steps above.
- Please do not leave waste, samples, or lab materials in the Characterization lab.
- OPUS is available free of charge. Please do not stay on the FTIR computer to do analysis.

Pellets:

In many cases it is preferable to use KBr pellets for powders. A blank KBr pellet is required for the back ground. Materials to make your pellets are not provided but we do have a hydraulic press you may use after training.

A typical press and die. This set is Available from across international: http://www.acrossinternational.com/13mm-1-2-Diameter-ID-Dry-Pressing-Die-Set-SDS13.htm



FTIR Pellet holder assembly

KBr is hydrophilic. The powder and any pellets should be kept in a dry place.

Fig. 12 – Pellet kit and holder assembly

The following procedure is taken from the MSE 313 Jr lab manual:

Note: FTIR is very sensitive to contaminants. You must wear gloves at all times. Also, do not use any lubricant on the pellet press. A hydrocarbon, such as steric acid, will seriously degrade any spectrum that is obtained, and using any in the press (die assembly) may require a replacement. ($500).

- Weigh out 200 mg of KBr. Add 1 mg of sample. Place the powders in the mortar and pestle. Grind up the powder until it is thoroughly mixed.
- Assemble the press. The silver "T" goes on the bottom. Put the silver collar on top. Put the small silver disk in the collar. Place the powder in the die. Put the plunger in. Make sure that the beveled part of the piston is on the outside of the press.
- Place the pellet press on the hydraulic press. Bring the pressure up to 15 psi for 60 seconds. Relieve the pressure in the press. Invert the die and use the collar to disgorge the pellet. Do this gently, since the KBr is very fragile.
- The FTIR machine is purged by passing nitrogen gas through the sample chamber. Put the plain KBr sample into the special holder.
- Wait for the CO2 peak to disappear and take a background. Remove the KBr pellet.
- Place the sample in the holder and again, wait for the CO2 peak to disappear.
- When ready, select “Sample Single Channel”
- If you have more than one sample, repeat the steps above.

Procedure for measurements using pellet holder:

- Follow the basic procedures indicated at the beginning of this SOP.
- Open the top of the sample chamber and pull out the pellet holder assembly (this is demonstrated during training).
- Install the blank KBr pellet.
- Monitor the spectrum signal until the CO2 peak is minimized.
- Select “Interferogram” then “Save Peak Position.
- Run a background.
- Open the top of the chamber to remove the holder assembly (immediately close to reduce exposure to lab air).
- Replace the blank KBr pellet with your sample pellet. (Remember to wear gloves!)
- Monitor the spectrum signal until the CO2 peak is minimized.
- Go back to the basic tab to run a sample scan.
- If you have multiple KBr samples you don’t have to do a new back ground each time if you run them quickly. If there is 30 minutes or more between scans it is probably a good idea to run a new background as changes in temperature or other ambient variables could have a small effect.

- When you have finished, please remove your samples and any lab waste to be disposed of in your own labs.
- Make sure the chamber is closed and close the sample chamber purge line (fig. 2).
- Save your data to USB for analysis.

Procedure for measurements using the EGA FTIR cell:

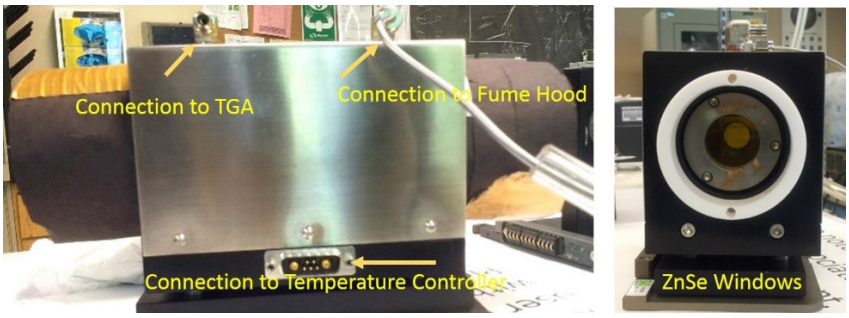


Fig. 13 EGA Cell

- Follow the basic procedures indicated at the beginning of this SOP. (The following procedures assumes the user has contacted lab personnel to install the cell).
- Open the "Chromatography" experiment file you created during training.
- Remember to change the scan starting range from 400 cm- to 600 cm-1.
- Monitor the spectrum signal while preparing the TGA program. (TGA training is separate).
- Tare the empty crucible then load sample as any standard TGA measurement.
- Note the time for the TGA scan and be sure to enter that value (+2min.) in the Advanced tab of the experiment file in FTIR Chromatography where it asks for minimum time.
- Do not start the TGA, but press the "Sample" button on the instrument to load the crucible and raise the furnace.
- Leave the furnace raised so that the N2 purge through the furnace flows/purges the EGA cell. This can take up to 30 minutes.
- Make sure that both the line and the cell temperatures are up to at least 198 C. (controller will be turned on by lab personnel during regular EGA cell installation.)
- When CO2 peak is minimized (it won't be completely eliminated) Select "Interferogram" then "Save Peak Position.
- Run a background.
- Start the FTIR scan and wait for the 3-d graph to appear.

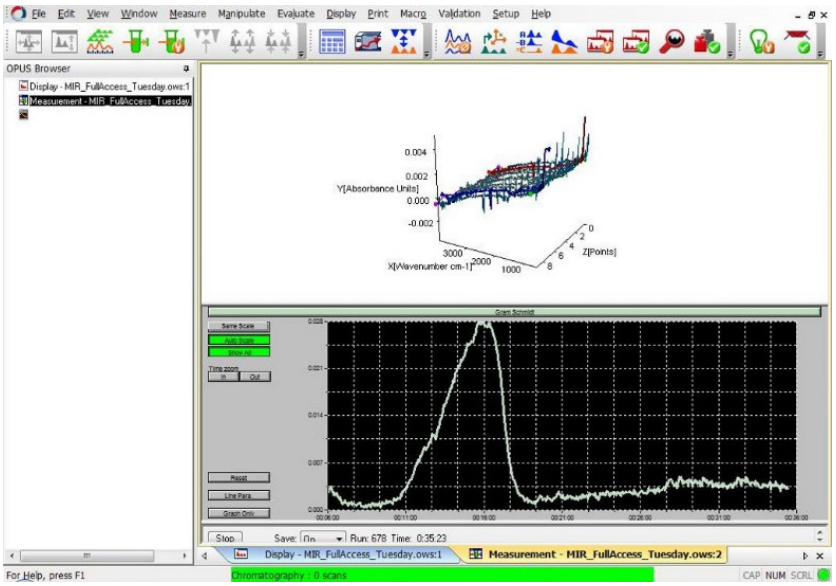


Fig. 14 OPUS 3D scan. Shows scan after 40 minutes. Peak is the Gram Schmidt

- Start the TGA.
- The two programs will run in tandem.

TGA-FTIR data extraction:

During the time that this measurement is done, the FTIR software can save up to 4000 spectra. This is an enormous amount of data and generally all one needs is the spectra for the highest concentration of decomposition gas. To extract these spectra, use the following procedure. For more detailed analysis, help please use the interactive software and help files that load with your OPUS software as well as the tutorial recommended from the TA Instruments web page. ***Please follow these procedures on your lab computer and not on the FTIR/TGA computer as this computer if for operation and data collection only.***

- Open Universal analysis and load the TGA data.
- Under the Signals tab add the derivative with respect to temperature

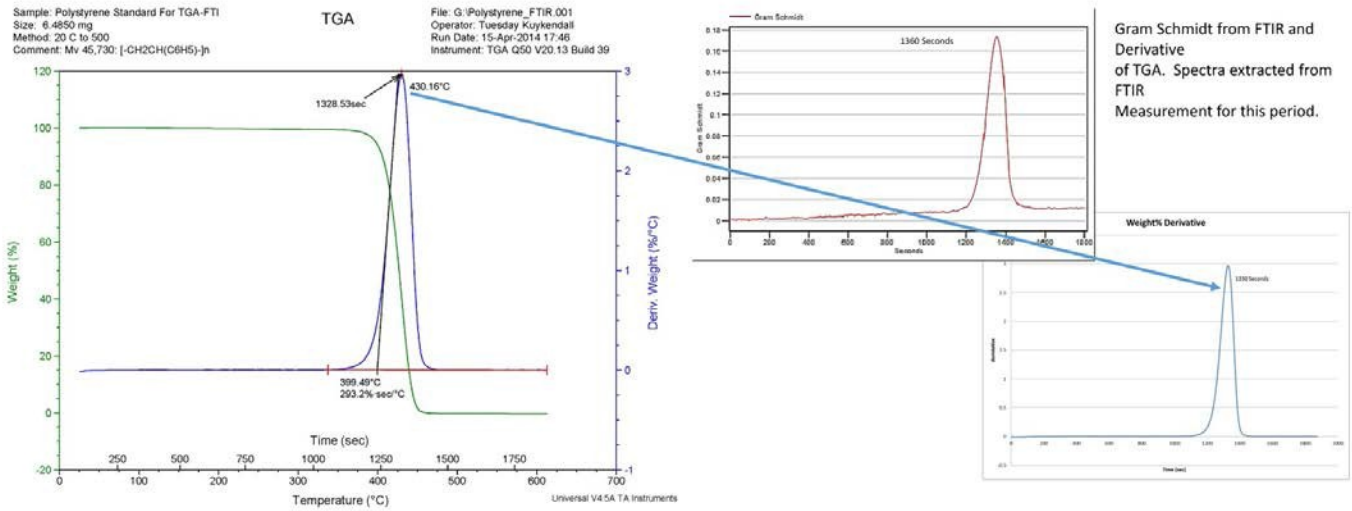


Fig. 15 Comparison of Gram Schmidt and Wt. % derivative of Polystyrene Decomposition

- A second graph will be overlaid on the original graph and there should be a distinct peak
- Determine the time (in seconds) at the peak maximum.
- Open the 3-D window in OPUS and load your sample file.
- From the spectra list select about 50 spectra around the peak time determined above.
- Right click on this selection and 'extract selected spectra'.
- The selected spectra will be listed in a new window.
- You can average all of this spectra to gain a single spectrum for further analysis.

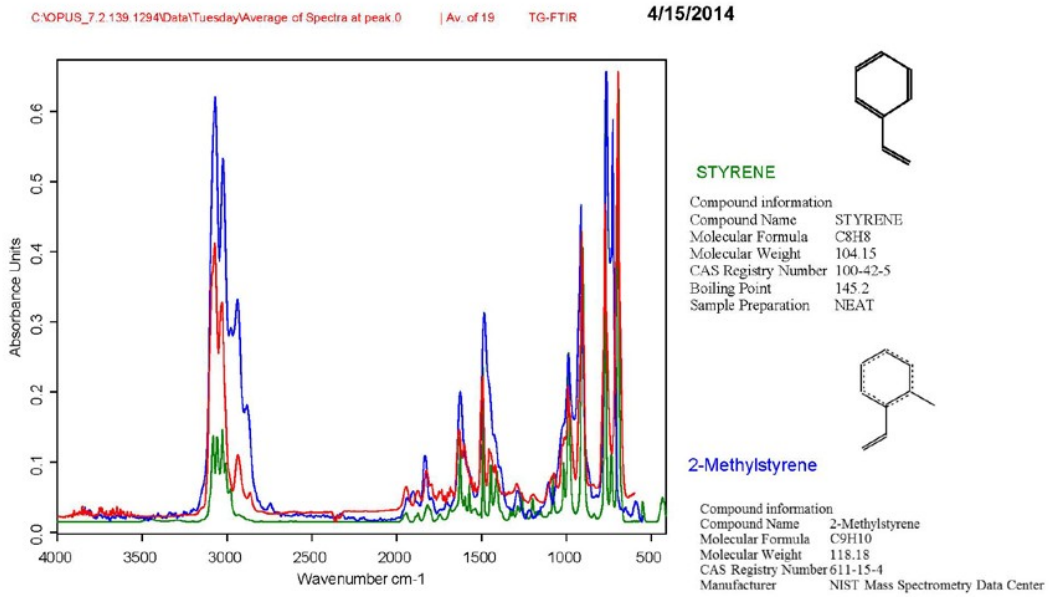


Fig. 16 The red graph is the average of all the spectra taken around 1300 – 1400 seconds. The blue and green graphs are the spectra search results. These were copied from OPUS and pasted into a power point slide for the report.