

A5

A5-Nicolet iS5 Infrared Spectrometer with ATR

Operating the Spectrometer and Software

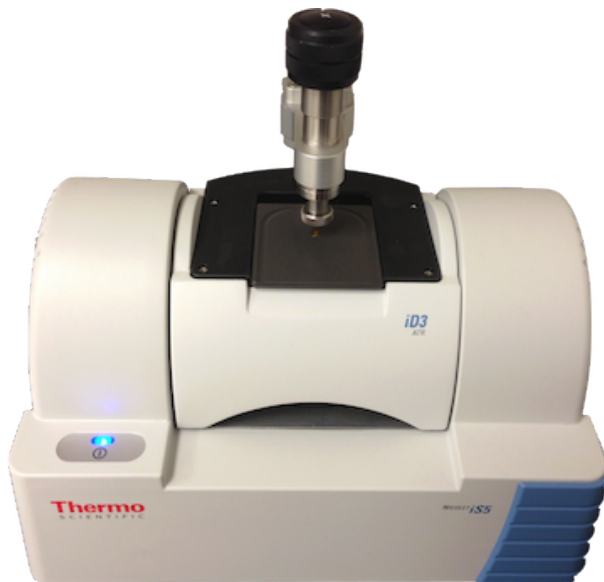


Figure A5.1: Nicolet iS5 Infrared Spectrometer with ATR Accessory.

LOCATION

Organic Chemistry Laboratory: A242 RHC Campus (Skokie).

PROTECT THE CRYSTAL!

The iD3 attenuated total reflectance (ATR) accessory contains a Zn-Se crystal, which is fairly soft (knoop# = 137 compared to 7000 for diamond).

- Do not clean the attenuated total reflectance (ATR) crystal with laboratory wipes (e.g., kimwipes) or paper towels. Doing so will scratch and ruin the crystal. Only use a soft cloth, cotton balls or cotton swabs.
- Do not clean the crystal with acetone. Doing so may damage the crystal epoxy. Use absolute ethanol, isopropanol or methanol.
- Do not use strong acids or bases.
- Ensure solid samples are soft or smooth (e.g, piece of plastic bottle is fine). Grind crystalline solids in a mortar first.
- Do not apply pressure device directly to the crystal without a sample.
- Do not drag pressure device across crystal. Turn counterclockwise first.

SETUP

1. Ensure that the IR is on (it should always be on). The blue light on the left will be illuminated.
2. Log-in to the **CHEMISTRY** account (no password).

Spectral Range

The spectral range of ZnSe is 20,000-550 cm^{-1} .



OMNIC Desktop Icon



Toolbar Icons

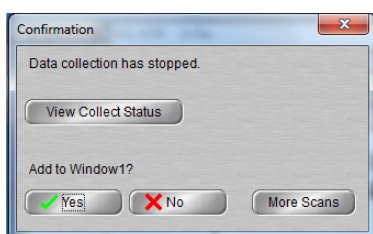
Expt Set: Experiment Setup
Col Bkg: Collect Background
Col Smp: Collect Sample

3. Open the **OMNIC** software from the desktop icon.
4. When prompted for experiment type, select **ID3-ATR ZNSE**.
5. Optional: Load a saved configuration to ensure all spectral colors will show up when printing (black). Go to **FILE → OPEN CONFIGURATION** then choose **OAKTONORGO.CON**.
6. Optional: Change the experiment setup. This should not be necessary if no changes are made in between classes, even if the software is closed. Click on the **EXPTSET** icon or go to **FILE → EXPERIMENT SETUP**. Change the **NO. OF SCANS** to 8-64 (8 is usually sufficient). Change **FINAL FORMAT** to %Transmittance.

ACQUIRE BACKGROUND

A background does not need to be collected before every sample acquisition, but it must be collected before the first sample acquisition after opening the software. The software will ask for a new background after every 120 minutes.

1. Ensure the crystal is clean and that the pressure device is not in contact with the crystal.
2. Click the **COLBKG** icon or go to **COLLECT → COLLECT BACKGROUND . . .** You may view the scan progress in the lower left of the screen.
3. When prompted to add the background to the current window, click **NO** unless you also want to print out the background or view the background first. If you select **YES**, you may hide the background later. (See **MULTIPLE SPECTRA** below).



Add-to-Window Prompt

APPLY LIQUID SAMPLE

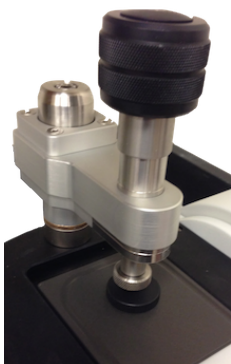
1. Add a small drop of liquid to the crystal with a pipette.
2. Optional: For volatile liquids, place the volatiles cover over the crystal with the O-ring facing down.
3. Optional: Gently apply the pressure device to the volatiles cover to hold it in place. Do not apply the pressure device to the crystal if you are not using the volatiles cover.
4. If the volatiles cover is not effective, slowly add drops of your sample during acquisition.

OR APPLY SOLID SAMPLE

1. Add a small portion of solid to the crystal with a spatula. The solid should be soft and powdered to prevent scratching the crystal.
2. Swing the pressure device over the crystal and turn the knob clockwise until the cross hairs on the pressure tower stop spinning. You cannot over tighten the device.

ACQUIRE DATA

1. Click the **COLSMP** icon or go to **COLLECT → COLLECT SAMPLE . . .**
2. When prompted, enter a title for the spectrum. You may change the title later by selecting the spectrum and clicking in the navigation bar.
3. When prompted to add the spectrum to a window, click **YES**.



Using the Volatiles Cover

The pressure device is applied to volatiles cover after application of a liquid.



Navigation Bar



Clear Icon

MULTIPLE SPECTRA

You may acquire additional spectra or open a saved spectrum and add to the same window. To overlay the spectra go to **VIEW → OVERLAY SPECTRA**. To stack spectra go to **VIEW → STACK SPECTRA**. To hide a spectrum, select it by left clicking on it, and then go to **VIEW → HIDE SPECTRA**. To show a hidden spectrum, left click the arrow next to the navigation bar and choose the spectrum. To delete a spectrum, select it with the mouse, and then click the **CLEAR** icon; this cannot be undone.

PEAK PICKING

Threshold Method:

1. Select spectrum by left clicking.
2. Go to **ANALYZE → FIND PEAKS**
3. Using the mouse, left click anywhere in the spectrum to choose the threshold on the y-axis.
4. Adjust the sensitivity scroll bar to the left until desired peaks are picked.
5. Click the arrow to the right of the navigation bar and choose **REPLACE ORIGINAL SPECTRUM**.

Individual Annotate Method:

1. Click the annotate icon (**T**) in the toolbar at the bottom left of the screen.
2. Using the mouse, left click the spectral position you want to annotate. The frequency value is shown automatically.
3. Type in text if you wish to replace the frequency value.



PRINTING

With Titles, Name(s) and Date:

1. Go to **Report → Preview/Print Report**.
2. When prompted, enter analyst name(s) if desired. Otherwise just press return to skip.
3. View the report. Then click **PRINT**. If the Oakton report was not already loaded, first go to **REPORT → TEMPLATE**, and then choose **OAKTONORGO.RPT**. Repeat steps 1-3.

With No Titles or Formatting:

1. Go to **FILE → PRINT** and then select **DELL 1110**. You may have to scroll over to view the printer.
2. Click **PRINT**.

SAVING

1. Select spectrum to be saved by left clicking with the mouse. (Only one spectrum may be saved at a time.)
2. Go to **SAVE → SAVE AS**.

What is Attenuated Total Reflectance Anyway?

Whatever it is, it's amazing! The attenuated total reflectance (ATR) accessory allows us to acquire spectra in a matter of seconds. The reason? There is little sample preparation required. Just apply the sample to the crystal surface, apply pressure if it's a solid, start scanning, and voila. Compare this to transmission infrared (IR) spectroscopy. Here the sample must be transparent since the infrared beam will be passing through it. That's usually not a problem in the case of liquids. For solids, however, you would either need to prepare a solution or use a number of more complex techniques such as dispersing the solid in KBr pellets or Nujol mulls. As light passes through the sample, specific frequencies of infrared light are absorbed corresponding to the frequency of molecular bond movements such as stretching and bending.

In ATR, the IR beam does not pass through the sample, but rather is reflected off the sample (Figure A5.2). As long as the refractive index of the crystal is greater than that of the sample and the IR beam enters at an angle greater than the critical angle, total internal reflectance occurs. As the light bounces off the inside of the crystal surface, a small amount of radiation penetrates the sample and then returns to the reflected IR beam. Since the intensity of this light decays exponentially (an evanescent wave) it can only penetrate the sample a few micrometers (μm). (For comparison, the diameter of a human hair is 17-180 micrometers.) This is the reason solids must be compressed onto the crystal surface, to ensure there is no air gap between the crystal and solid.

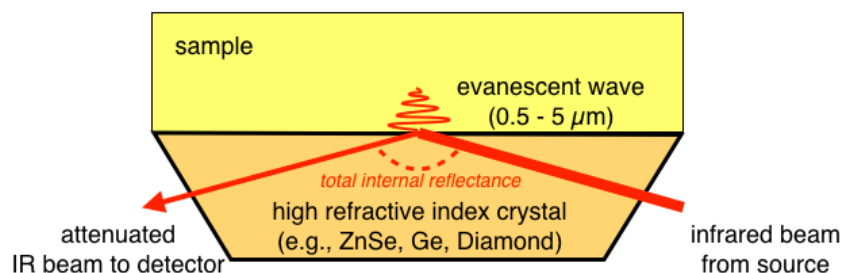


Figure A5.2: Evanescent wave upon total internal reflection of infrared beam.

The energy of the evanescent wave is attenuated (magnitude decreased) by absorption of the characteristic vibrational frequencies of the sample. The attenuated wave then returns to the path of the IR beam and continues to the detector.

COMPARISON OF ATR AND TRANSMISSION SPECTRA

Despite the drastically reduced sampling time, ATR spectroscopy does present some challenges. The spectrum obtained from ATR spectroscopy is not identical to a spectrum obtained through transmission techniques. ATR causes reduced band intensities as well as small, but significant shifts in absolute frequency toward lower wavenumbers. If an ATR spectrum representative of a transmission spectrum is desired (e.g., for comparing to spectral libraries) the ATR spectrum should be *corrected*. After correction, the peak positions and intensities more closely resemble those of transmission data. However, a corrected ATR spectrum is still only an approximation of the data that would have been collected in transmission mode. It's important, therefore, to always list the method of acquisition when reporting IR data.