

How to: ATR spectroscopy

Darby Duffy

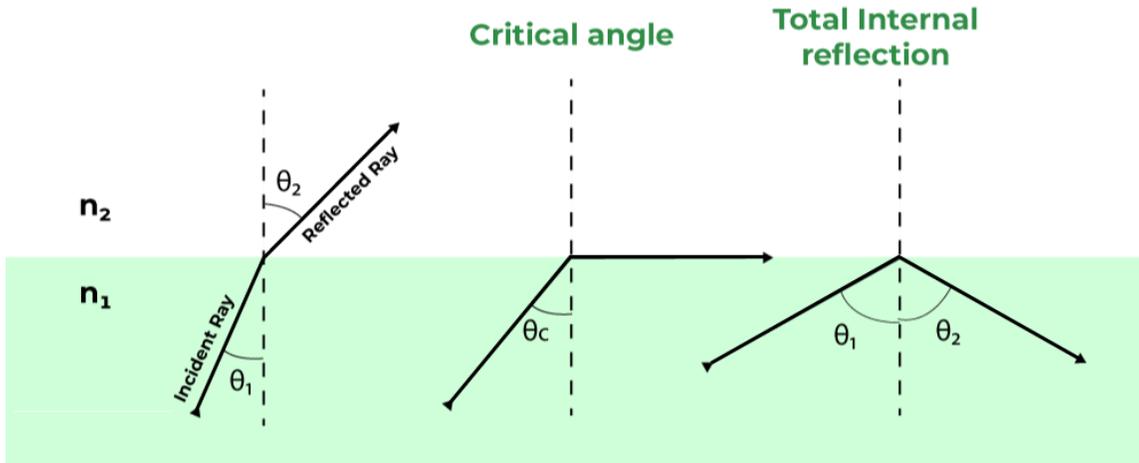
Jan 24, 2024

Thermo IS50 Advanced FTIR in our lab



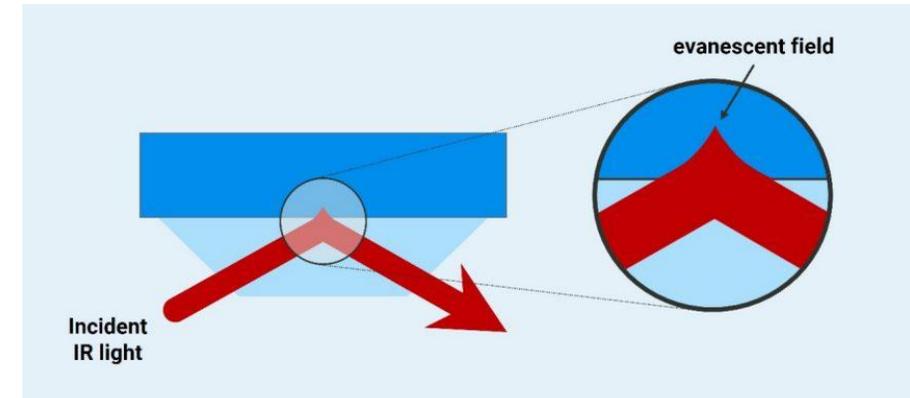
Attenuated Total Reflection (ATR) Spectroscopy

Total Internal Reflection



Snell's law

$$\theta_c = \sin^{-1}(n_2/n_1)$$



Crystals have different refractive indexes as seen in the table, and most organic based samples are around 1.5

ATR has replaced a lot of transmission experiments, it requires little to no sample prep, can be done on a variety of samples, and can give same information as transmission IR spectroscopy.

Table 1 Common materials for ATR crystals; critical angle calculated for n2=1.5; table taken from Griffiths P.R., de Haseth J. A. (2007). Fourier Transform Infrared Spectrometry. New York, USA: John Wiley & Sons.

| Cell material | Refractive index | Critical angle (degrees) |
|----------------------|------------------|--------------------------|
| Silver chloride AgCl | 1.90 | 49° |
| KRS-5 | 2.37 | 40° |
| Zinc selenide (ZnSe) | 2.40 | 40° |
| Zinc sulfide (ZnS) | 2.2 | 43° |
| Germanium (Ge) | 4.00 | 22° |
| Silicon (Si) | 3.41 | 26° |
| Diamond | 2.41 | 40° |

<https://www.geeksforgeeks.org/total-internal-reflection/>

<https://www.labcompare.com/10-Featured-Articles/352695-Pathlength-Considerations-With-ATR-Sampling-in-FTIR/>

<https://www.bruker.com/en/products-and-solutions/infrared-and-raman/ft-ir-routine-spectrometer/what-is-ft-ir-spectroscopy/atr-attenuated-total-reflectance.html>

Thermo IS50 Advanced FTIR in our lab



Screws on 4 corners of baseplate to mount attachment into instrument. Adjustable to connect two sides of attachment.

There are other How To slides on the group website

How
Sp

Polarization Modulation Infrared Reflectance Absorption Spectroscopy (PMIRRAS)

18

Samantha Nania
Shaw Group Meeting
140908 How it Works



JACOB GRANT
Professor Scott Shaw Research Group
Group Meeting 141027



Turn on the instrument and gather supplies



Ethanol is used to clean the ATR crystal.

100 microliters is the typical liquid samples size.

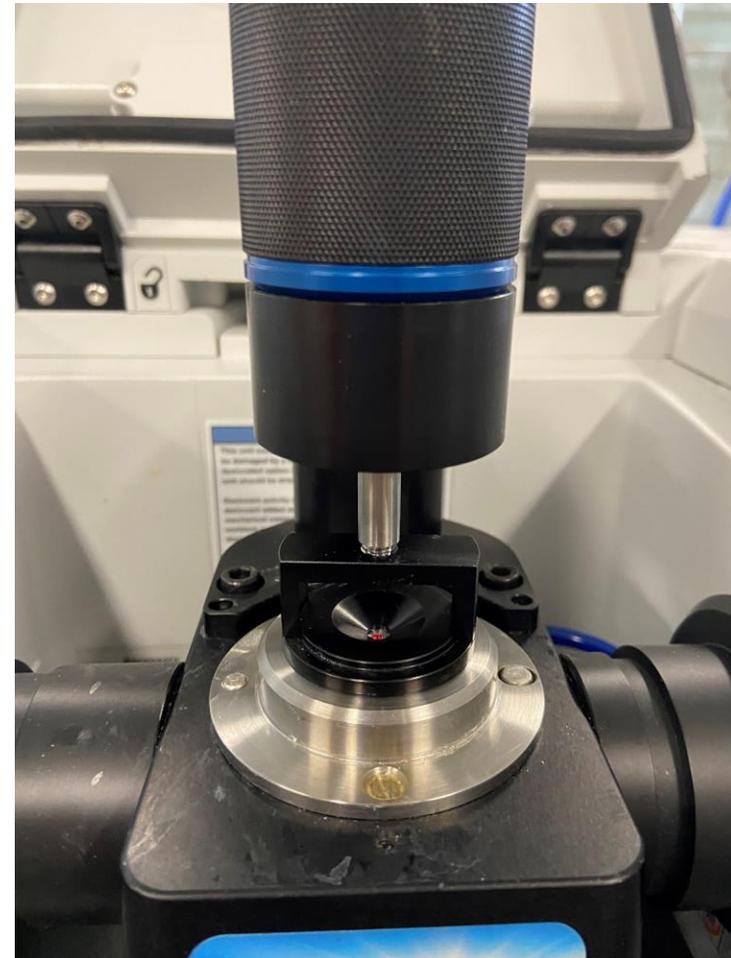
Chose your sample holder



Solid samples:

Small amount of sample needed.

Should probably be tested if it dissolves in ethanol to prevent contamination of future samples

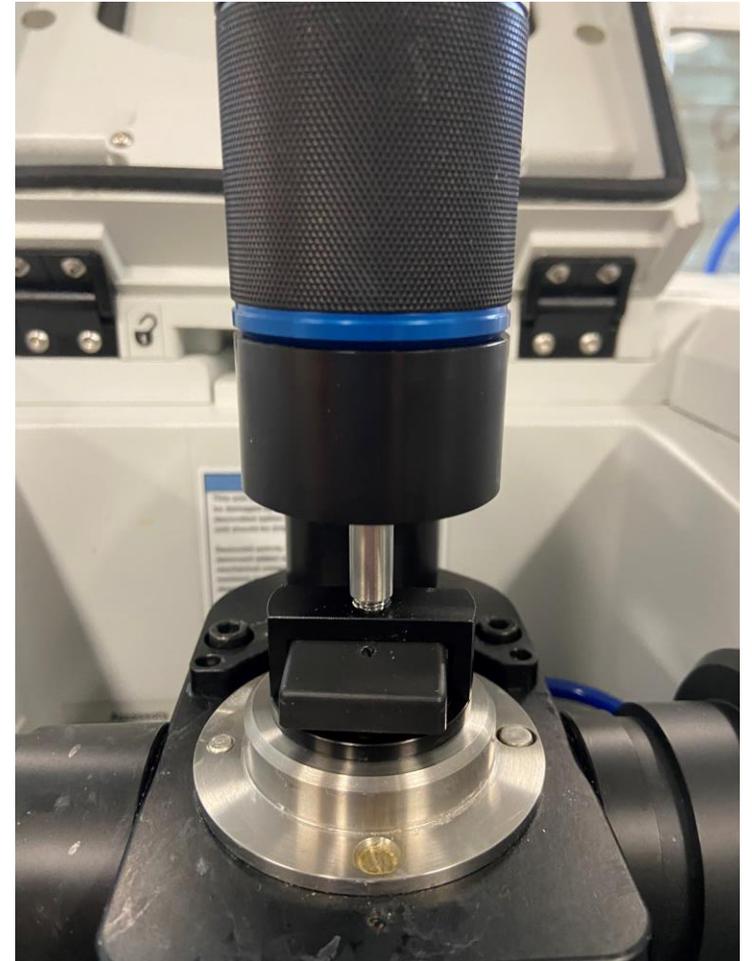
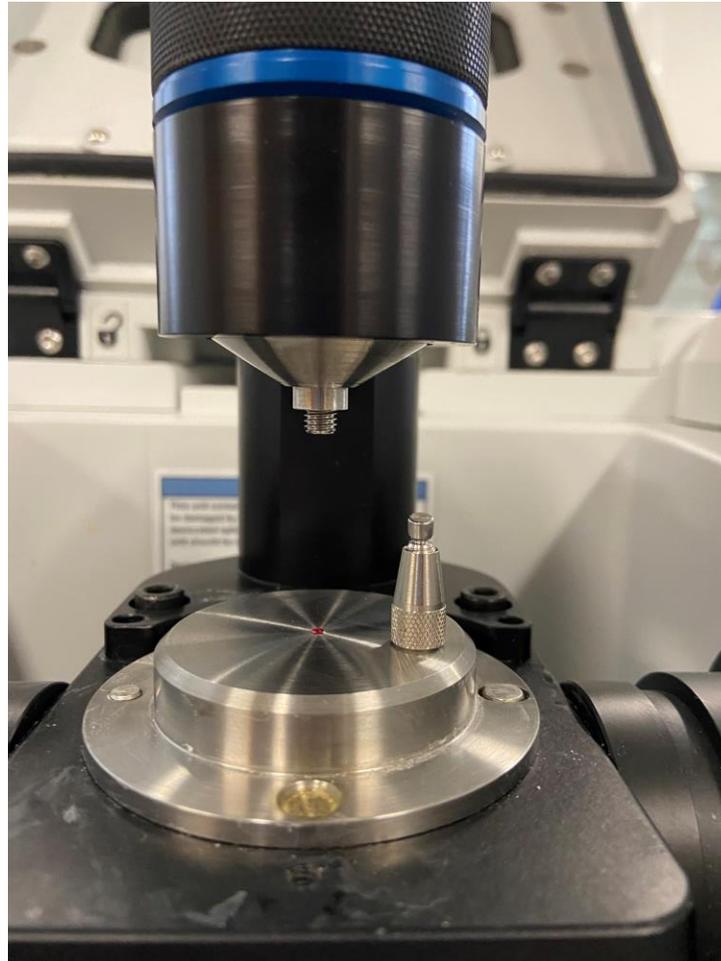
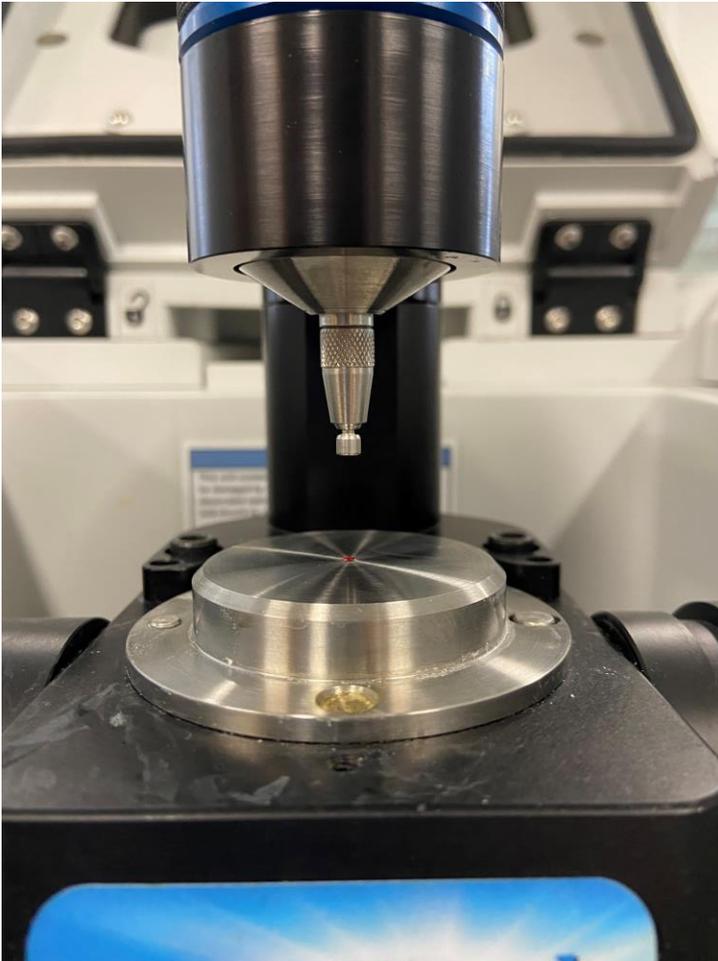


Liquid samples:

~100 microliters

How to change between solid and liquid samples

Cap helps prevent solvent evaporation



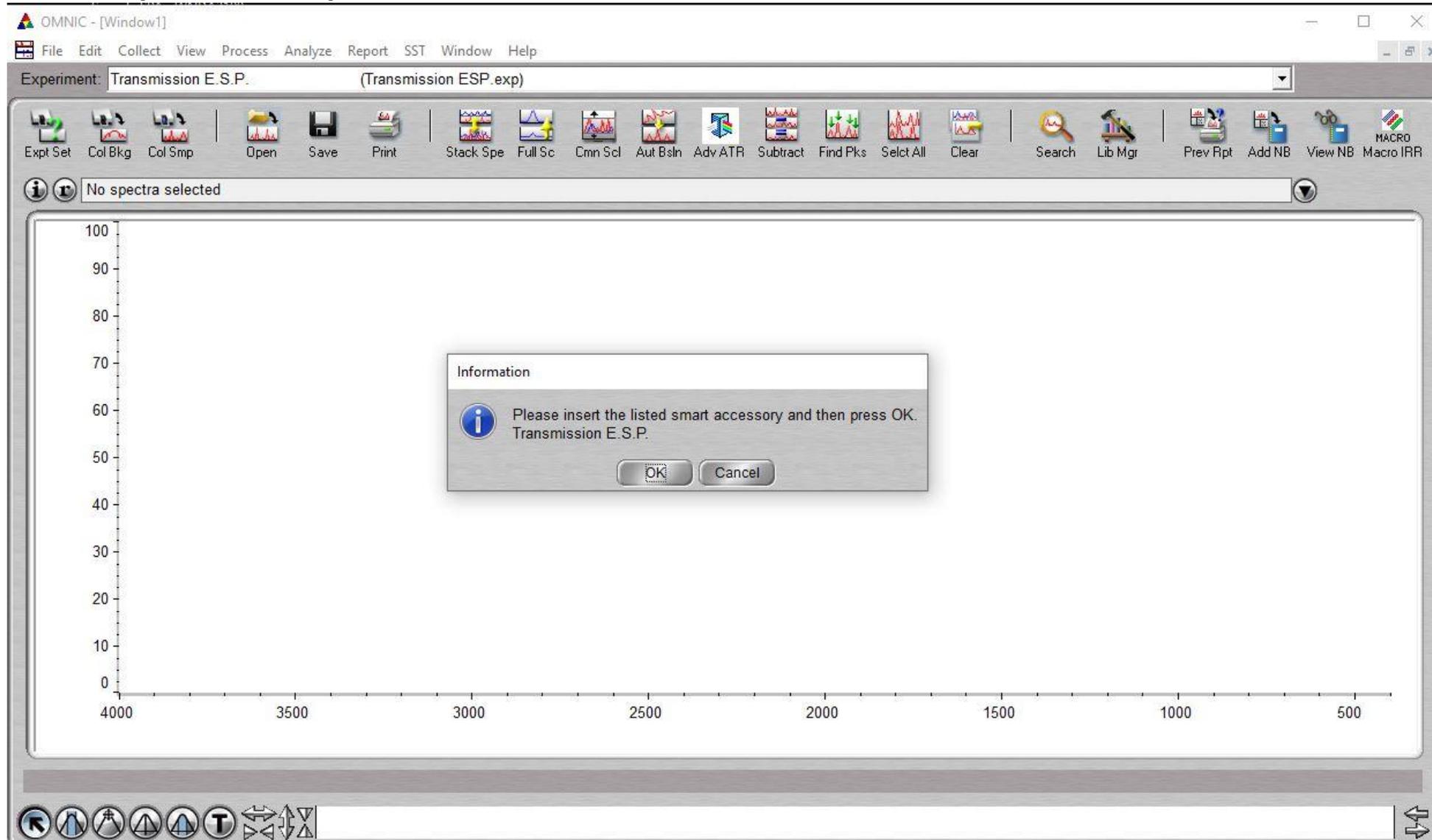
Software and where to save



The screenshot shows a Windows File Explorer window titled "IR Group Data-Thermo". The address bar indicates the path: "This PC > Local Disk (C:) > Shaw Group Data > IR Group Data-Thermo". The left sidebar shows the navigation pane with "Local Disk (C:)" selected. The main pane displays a list of files and folders with columns for Name, Date modified, Type, and Size.

| Name | Date modified | Type | Size |
|----------------------------|---------------------|-------------|--------|
| Former Group Members | 4/5/2022 2:42 PM | File folder | |
| Jess | 4/5/2022 2:43 PM | File folder | |
| Nathan | 4/5/2022 2:43 PM | File folder | |
| Niroodha | 4/5/2022 2:43 PM | File folder | |
| Rural Scholars | 4/5/2022 2:43 PM | File folder | |
| Test Data | 4/5/2022 2:43 PM | File folder | |
| Visitors | 4/5/2022 2:43 PM | File folder | |
| Chris | 6/6/2022 2:31 PM | File folder | |
| Andy | 6/12/2022 3:22 PM | File folder | |
| Sazzad | 7/13/2022 11:19 AM | File folder | |
| Janaka | 7/27/2022 12:59 PM | File folder | |
| Sanika | 9/21/2022 10:21 AM | File folder | |
| Grace | 12/29/2022 1:02 PM | File folder | |
| Whitney | 5/3/2023 2:12 PM | File folder | |
| Ramin IRRAS_PM_ATR | 5/23/2023 2:37 PM | File folder | |
| Colleen | 6/22/2023 1:58 PM | File folder | |
| Michael | 12/15/2023 12:02 PM | File folder | |
| Chamini | 1/20/2024 5:19 PM | File folder | |
| Darby | 1/22/2024 10:13 AM | File folder | |
| SKS | 3/25/2014 12:15 PM | Shortcut | 2 KB |
| Delay IRRAS.mac | 7/11/2016 5:03 PM | MAC File | 10 KB |
| Macro PMIRRAS.mac | 4/6/2017 5:44 PM | MAC File | 10 KB |
| Macro IRRAS background.mac | 11/15/2017 5:56 PM | MAC File | 10 KB |
| Test1 1 | 2/12/2018 4:34 PM | File | 158 KB |

When you open OMNIC- transmission is default



Change the experiment to iS50 ATR

The screenshot displays the OMNIC software interface. A blue arrow points to the 'Experiment: iS50 ATR' dropdown menu in the top toolbar. An information dialog box is open in the center of the plot area, containing the following text:

Information

Experiment file specifies DTGS ATR detector, but it is not available in Main sample location. DTGS KBr detector selected instead.

c:\my documents\omnic\param\Default iS50 ATR.exp

OK

The background plot area shows a y-axis from 0 to 100 and an x-axis from 4000 to 500. The status bar at the bottom indicates 'No spectra selected'.

Collect > experiment set up

Adjust for resolution

Background options

OMNIC

File Edit Collect View Process Analyze Report SST Window Help

Experiment: iS50 ATR (Default iS50 ATR.exp)

Expt Set Col Bkg Col Smp Open Save Print Stack Spe Full Sc Cmn Scl Aut Bshl Adv ATR Subtract Find Pks Sclt All Clear Search Lib Mgr Prev Rpt Add NB View NB Macro IRR

Experiment Setup - c:\my documents\omnic\param\Default iS50 ATR.exp

Collect Bench Quality Advanced Diagnostic Configure

Estimated time for this collection: 00:00:47

No. of scans: 32

Resolution: 4

Data spacing: 0.482 cm-1

Final format: Absorbance

Correction: None

Automatic atmospheric suppression

Preview data collection

Use transmittance data during preview

Use fixed Y-axis limits in collect window

Min: 0.00 Max: 2.00

Experiment title: iS50 ATR

File Handling

Save automatically Save interferograms

Base name: [dropdown]

c:\my documents\omnic\autosave\0001.spa

Background Handling

Collect background before every sample

Collect background after every sample

Collect background after 120 minutes

Use specified background file:

[text field] Browse...

Collect 64 scans for the background

Experiment description: Default experiment file for iS50 ATR

Help Open Save Save As OK Cancel

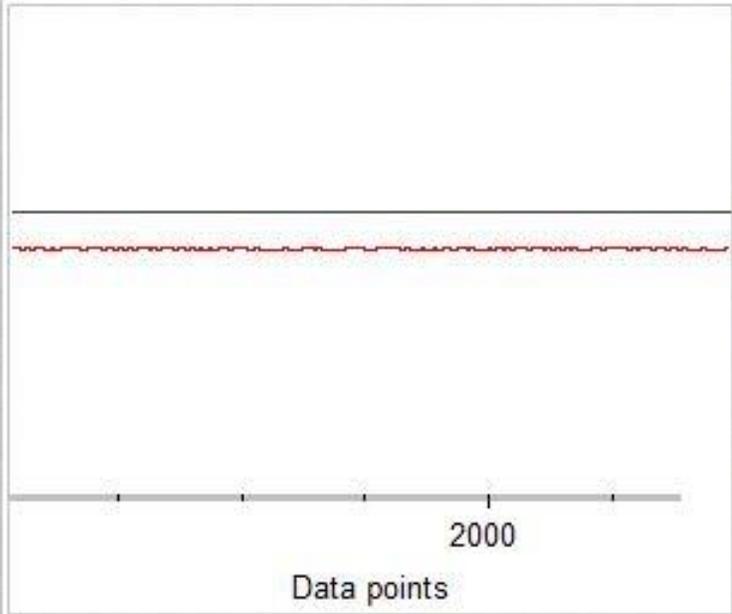
Bench tab- peak to peak

Experiment Setup - c:\my documents\omnic\param\Default i550 ATR.exp

Collect **Bench** Quality Advanced Diagnostic Configure

Peak to Peak:0.01 Loc:2046

Min/Max Peak to peak



2000
Data points

| Parameter | Value |
|--------------------|--------------------------|
| Sample compartment | Main |
| Detector | MCT/A |
| Beamsplitter | KBr |
| Source | IR |
| Accessory | None |
| Window | None |
| Recommended range | 4000 --- 650 |
| Max range limit | 4000 |
| Min range limit | 650 |
| Gain:1 | 1.0 |
| Optical velocity | 1.8988 |
| Aperture | 25 |
| Sample shuttle | <input type="checkbox"/> |
| Attenuation | None |

Freeze Single beam Tone

Help Open Save Save As OK Cancel

Change to
MCT/A

Experiment Setup - c:\my documents\omnic\param\Default iS50 ATR.exp



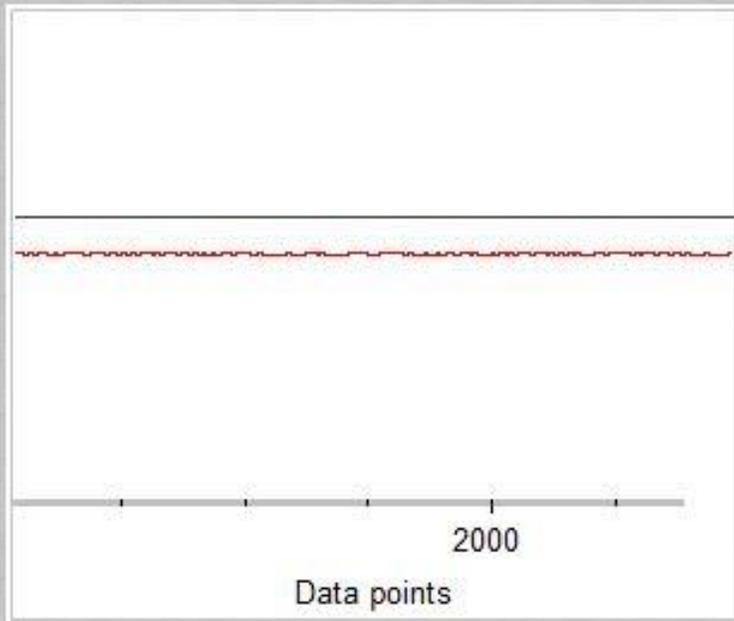
Collect Bench Quality Advanced Diagnostic Configure



Peak to Peak:0.01 Loc:2046

Min/Max

Peak to peak



Freeze

Single beam

Tone

| Parameter | Value |
|--------------------|--------------------------|
| Sample compartment | Main |
| Detector | MCT/A |
| Beamsplitter | KBr |
| Source | IR |
| Accessory | None |
| Window | None |
| Recommended range | 4000 ---- 650 |
| Max range limit | 4000 |
| Min range limit | 650 |
| Gain:1 | 1.0 |
| Optical velocity | 1.8988 |
| Aperture | 25 |
| Sample shuttle | <input type="checkbox"/> |
| Attenuation | None |

Help

Open

Save

Save As

OK

Cancel



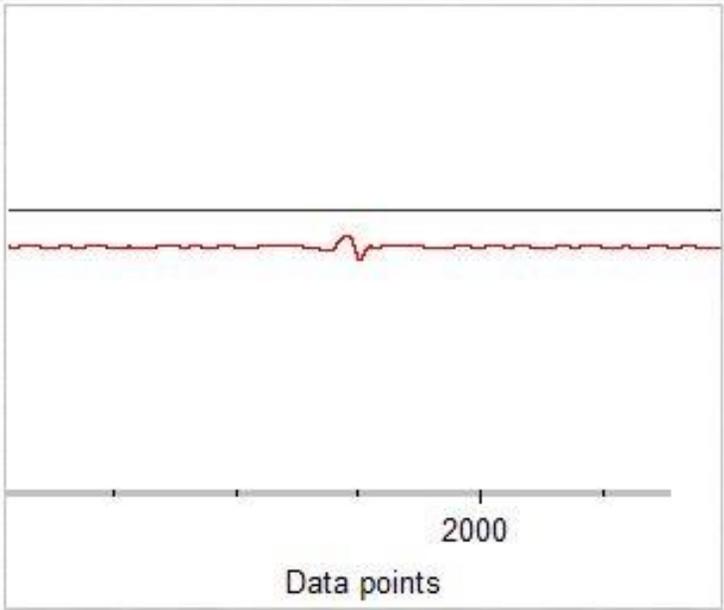
As we add liquid nitrogen, we can see the signal increase.

Experiment Setup - c:\my documents\omnic\param\Default iS50 ATR.exp

Collect Bench Quality Advanced Diagnostic Configure

Peak to Peak:1.06 Loc:2043

Min/Max Peak to peak



2000
Data points

| Parameter | Value |
|--------------------|--------------------------|
| Sample compartment | Main |
| Detector | MCT/A |
| Beamsplitter | KBr |
| Source | IR |
| Accessory | None |
| Window | None |
| Recommended range | 4000 ---- 650 |
| Max range limit | 4000 |
| Min range limit | 650 |
| Gain:1 | 1.0 |
| Optical velocity | 1.8988 |
| Aperture | 25 |
| Sample shuttle | <input type="checkbox"/> |
| Attenuation | None |

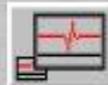
Freeze Single beam Tone

Help Open Save Save As OK Cancel

Experiment Setup - c:\my documents\omnic\param\Default i550 ATR.exp

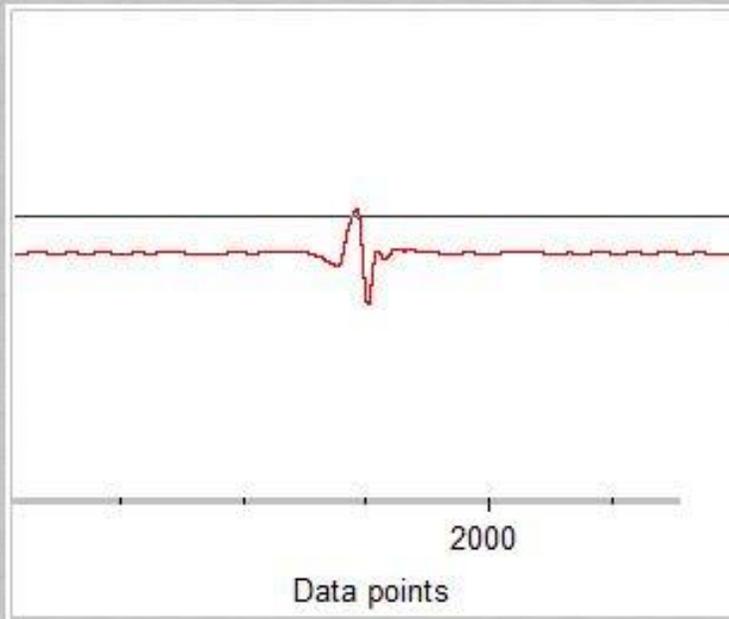


Collect Bench Quality Advanced Diagnostic Configure



Peak to Peak:3.91 Loc:2043

Min/Max Peak to peak



Navigation icons: left, right, up, down, zoom in, zoom out, and a vertical line with a red peak.

Single beam
 Tone

Freeze

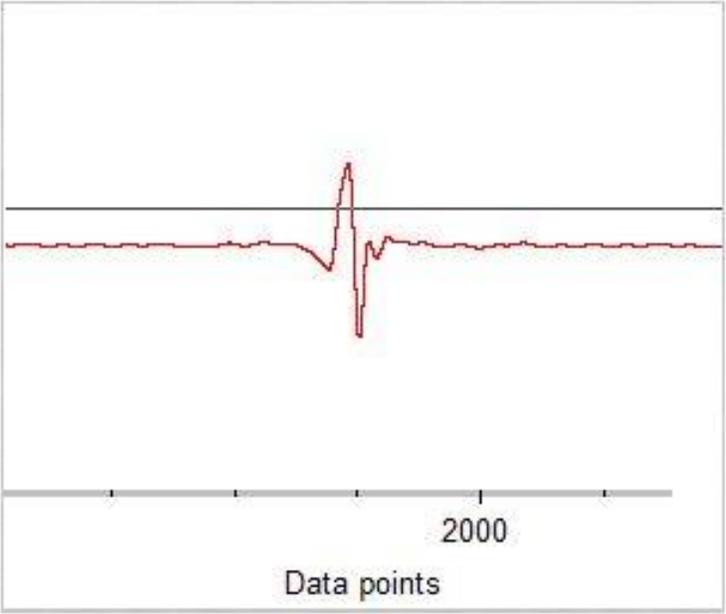
| Parameter | Value |
|--------------------|--------------------------|
| Sample compartment | Main |
| Detector | MCT/A |
| Beamsplitter | KBr |
| Source | IR |
| Accessory | None |
| Window | None |
| Recommended range | 4000 --- 650 |
| Max range limit | 4000 |
| Min range limit | 650 |
| Gain:1 | 1.0 |
| Optical velocity | 1.8988 |
| Aperture | 25 |
| Sample shuttle | <input type="checkbox"/> |
| Attenuation | None |

Help Open Save Save As OK Cancel

Experiment Setup - c:\my documents\omnic\param\Default iS50 ATR.exp

Collect Bench Quality Advanced Diagnostic **Configure**

 **Peak to Peak:7.28 Loc:2043**
 Min/Max Peak to peak



2000
Data points



Single beam
 Tone

Freeze

| Parameter | Value |
|--------------------|--------------------------|
| Sample compartment | Main |
| Detector | MCT/A |
| Beamsplitter | KBr |
| Source | IR |
| Accessory | None |
| Window | None |
| Recommended range | 4000 ---- 650 |
| Max range limit | 4000 |
| Min range limit | 650 |
| Gain:1 | 1.0 |
| Optical velocity | 1.8988 |
| Aperture | 25 |
| Sample shuttle | <input type="checkbox"/> |
| Attenuation | None |

Help Open Save Save As OK Cancel

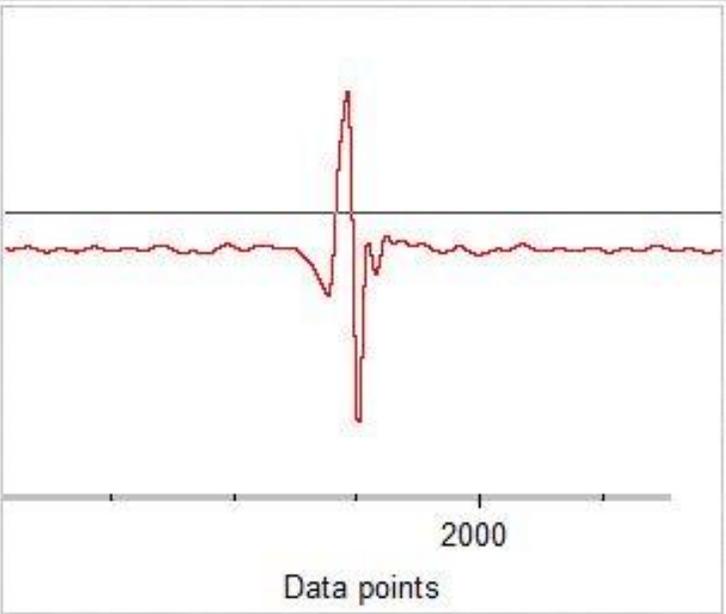
Write this down

Experiment Setup - c:\my documents\omnic\param\Default iS50 ATR.exp

Collect Bench Quality Advanced Diagnostic Configure

Peak to Peak:13.74 Loc:2043

Min/Max Peak to peak



2000
Data points

| Parameter | Value |
|--------------------|--------------------------|
| Sample compartment | Main |
| Detector | MCT/A |
| Beamsplitter | KBr |
| Source | IR |
| Accessory | None |
| Window | None |
| Recommended range | 4000 ---- 650 |
| Max range limit | 4000 |
| Min range limit | 650 |
| Gain:1 | 1.0 |
| Optical velocity | 1.8988 |
| Aperture | 25 |
| Sample shuttle | <input type="checkbox"/> |
| Attenuation | None |

Freeze Single beam Tone

Help Open Save Save As OK Cancel

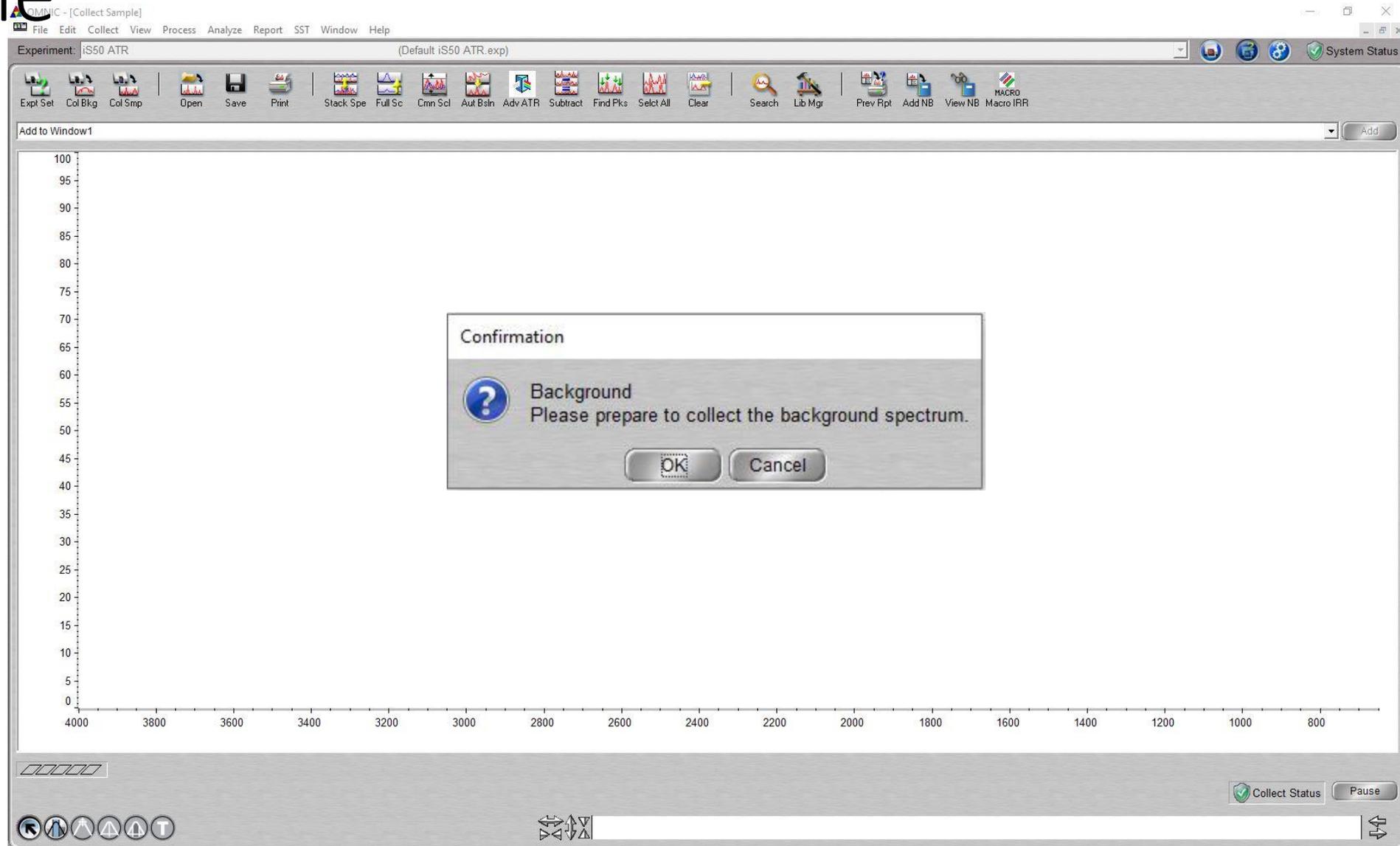
Let's take a measurement!

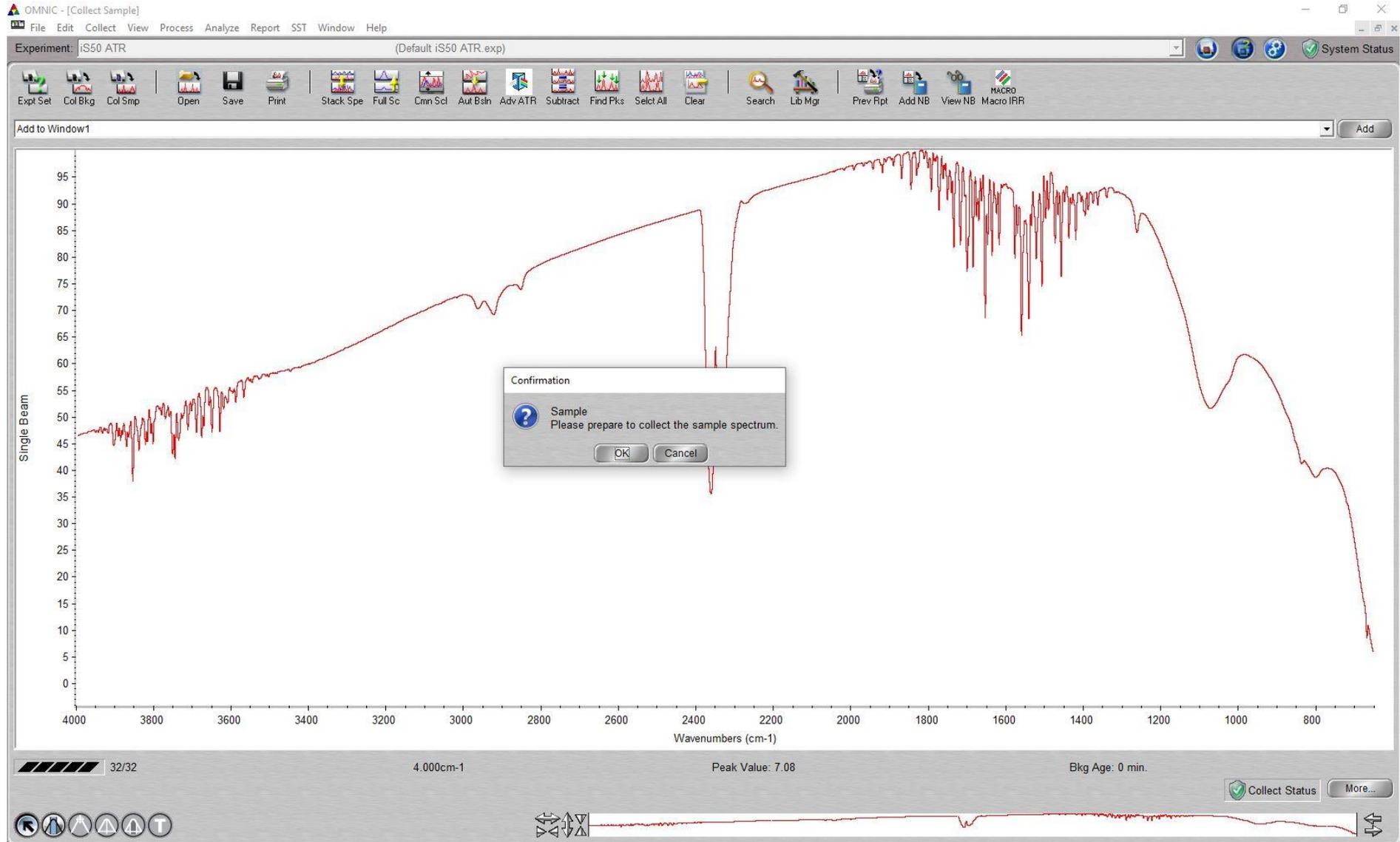
The screenshot displays the OMNIC software interface. At the top, the menu bar includes File, Edit, Collect, View, Process, Analyze, Report, SST, Window, and Help. The main toolbar contains various icons for file operations (Expt Set, Col Bkg, Col Smp, Open, Save, Print), data processing (Stack Spe, Full Sc, Cmn Sel, Aut Bsln, Adv ATR, Subtract, Find Pks, Sclt All, Clear), and analysis (Search, Lib Mgr, Prev Rpt, Add NB, View NB, Macro IRR). A status bar at the bottom right shows 'Collect Status' and 'Pause' buttons.

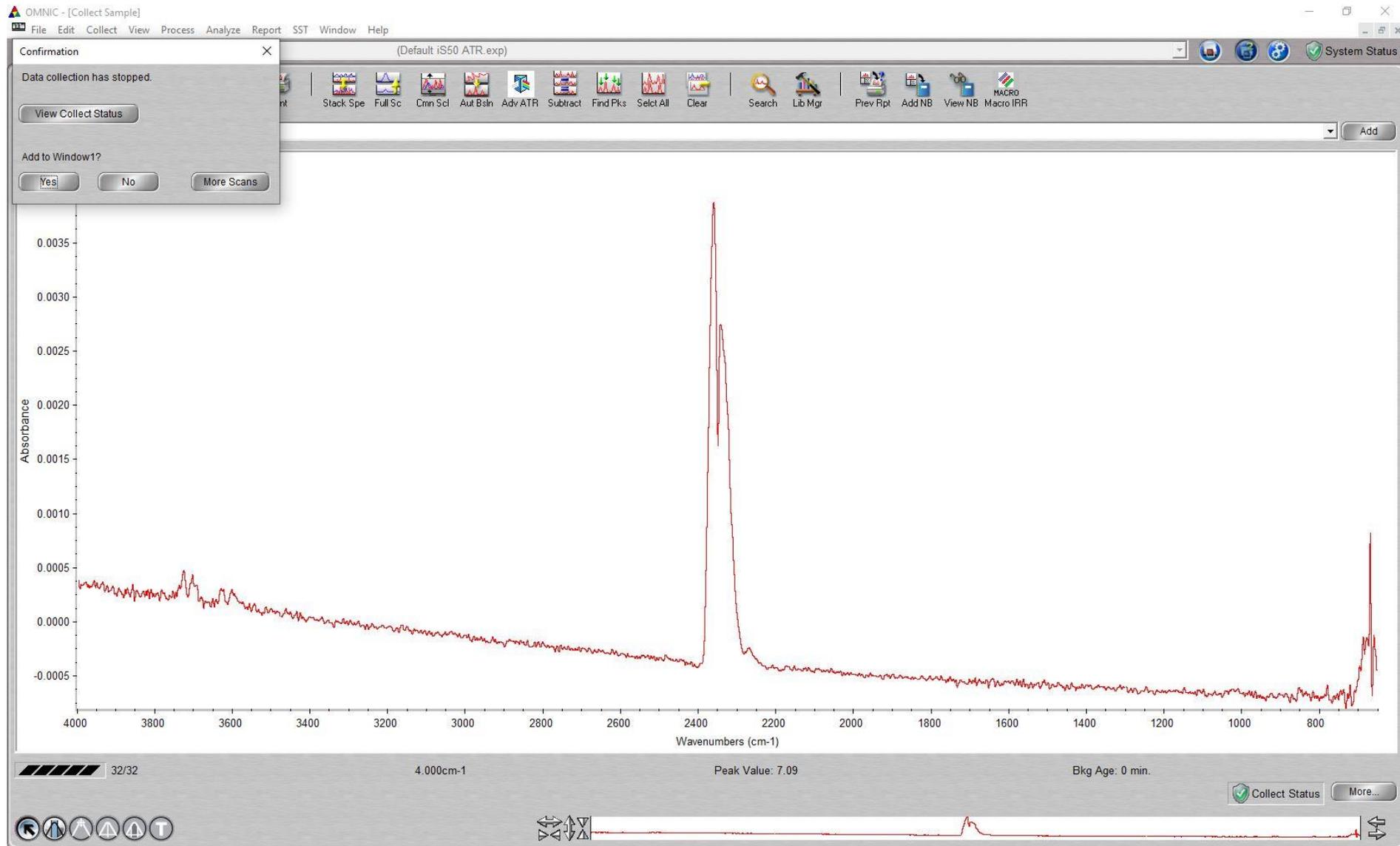
In the center, a 'Collect Sample' dialog box is open, prompting the user to 'Enter the spectrum title:'. The text field contains the timestamp 'Mon Jan 22 11:15:42 2024 (GMT-06:00)'. The dialog has 'OK' and 'Cancel' buttons.

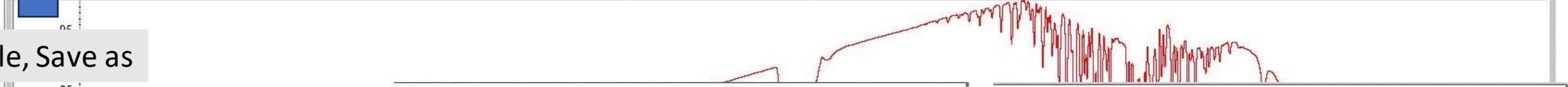
A blue callout box on the right side of the dialog contains the text: 'Should be descriptive, and consistent'. A blue arrow points from this callout box towards the 'Add to Window1' dropdown menu at the top left of the main plot area.

We selected “Collect background before every sample”









File, Save as

Save As - 01_dry ATR

Save in: how to

No items match your search.

File name: 01_dry ATR.SPA Save

Save as type: Spectra (*.SPA) Cancel

Read only

Set Filename to Title

Title: 01_dry ATR

Save As - 01_dry ATR

Save in: how to

No items match your search.

File name: 01_dry ATR.CSV Save

Save as type: CSV Text (*.CSV) Cancel

Read only

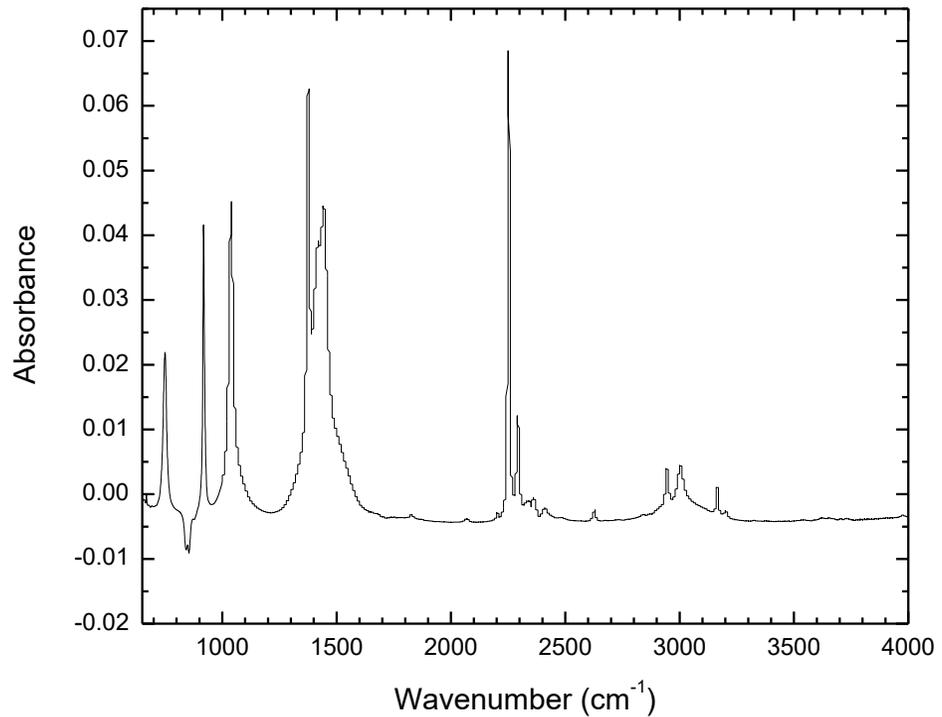
Set Filename to Title

Title: 01_dry ATR

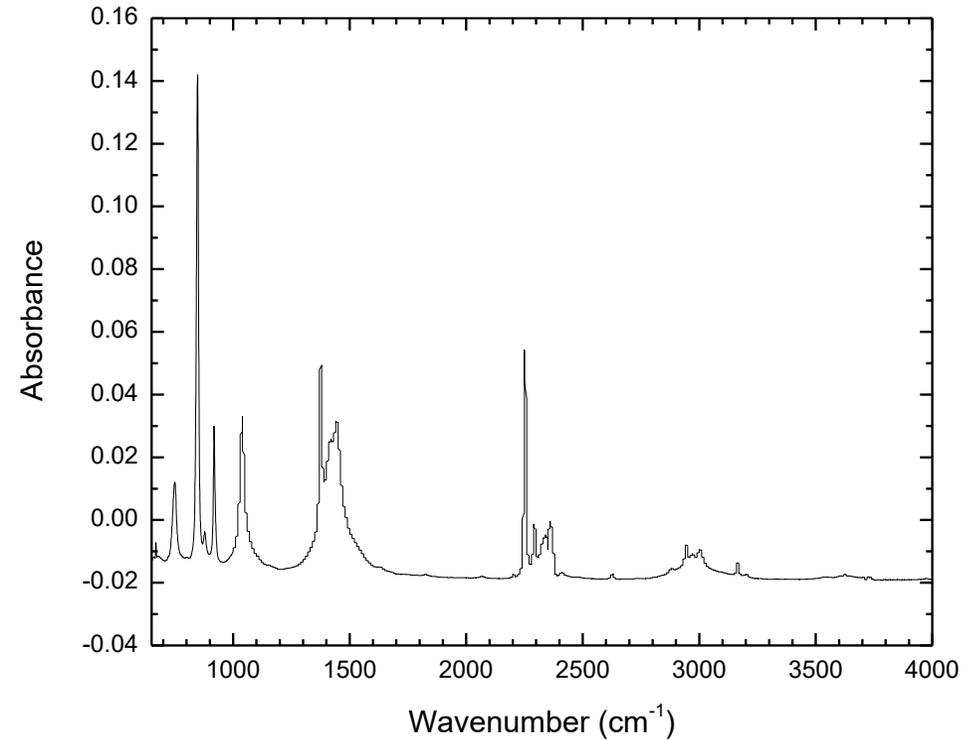


Examples of data

MeCN

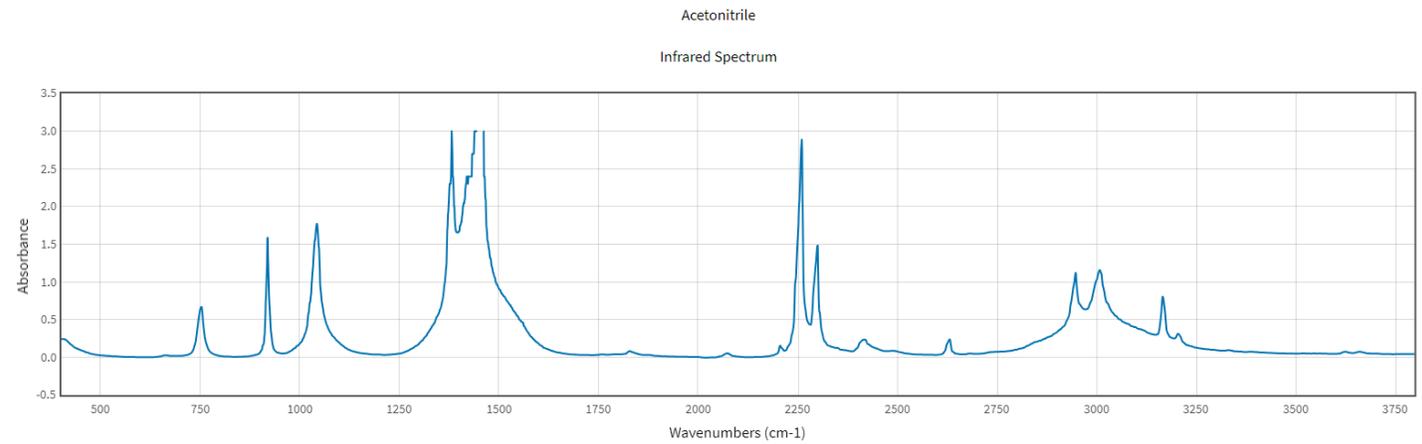
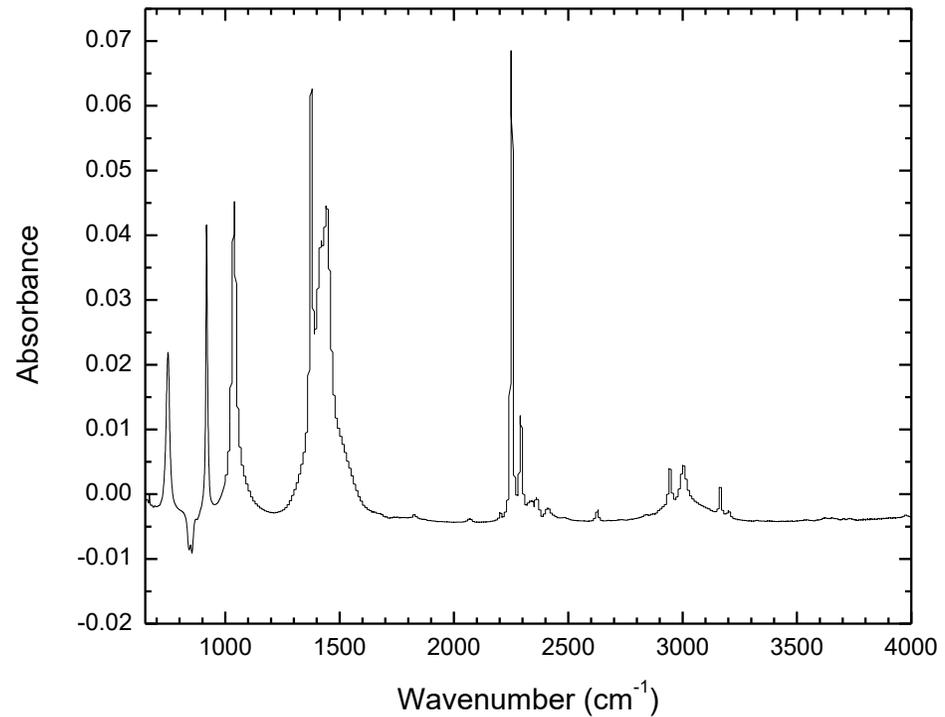


100 mM TBAPF₆ MeCN



Checking data with literature

MeCN



From NIST Chemistry WebBook

