SpecQuant Getting Started Guide

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Software Prerequisites

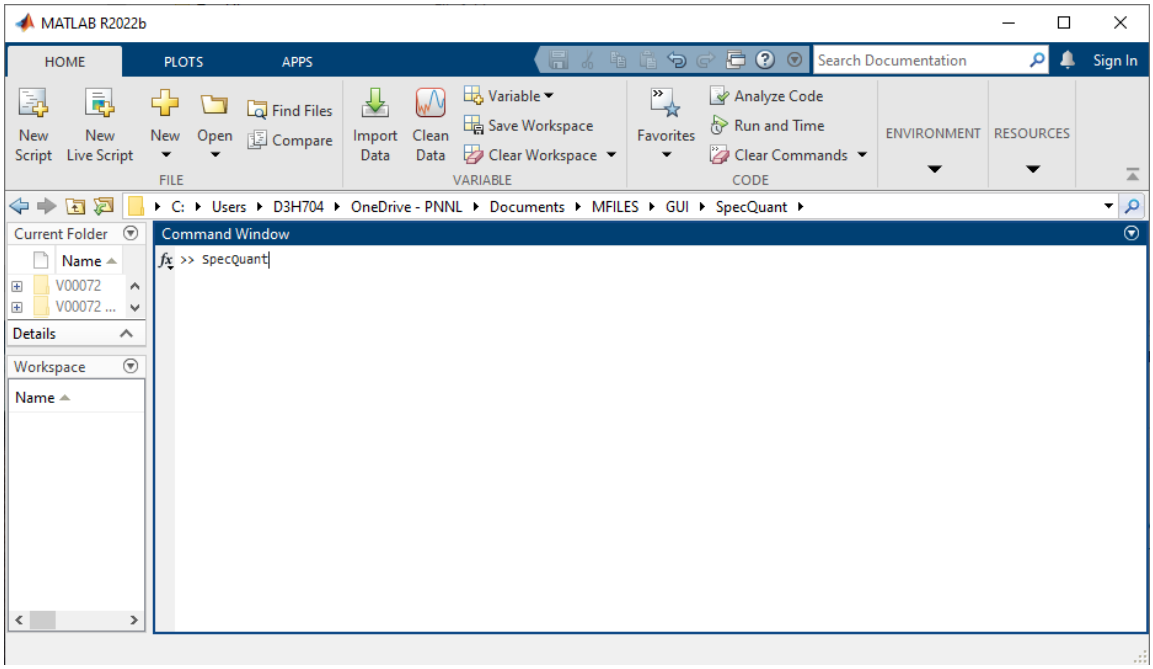
SpecQuant requires MATLAB version 2020b or higher (Mathworks; https://www.mathworks.com) and PLS_Toolbox version 9.1 or higher (Eigenvector Research, Inc.; https://eigenvector.com). Trial versions of these programs are available from their respective websites.

System Requirements

Refer to MATLAB's system requirements. SpecQuant has been tested on systems running Windows 10 and macOS 13 (Ventura).

Installation and Configuration

1. SpecQuant is packaged as a zip file. Extract the file's contents into a directory on your system. In these instructions, it will be assumed that the main program directory is named SpecQuant.
2. In MATLAB, add the following 3 directories to your MATLAB search path (see the MATLAB documentation for instructions on how to do this):
    a. SpecQuant (main program directory)
    b. SpecQuant\AppFiles
    c. SpecQuant\AuxFiles
3. Start MATLAB. Navigate to the SpecQuant main program directory, and enter "SpecQuant" at the MATLAB command line followed by <Enter>.



4. When SpecQuant's main window appears, click the Tools menu and select "Set Path for Spectrum Files…". When prompted, select a directory where spectrum files are stored on your

system. Some simulated spectra are included with SpecQuant for testing; if you wish to start with these data (recommended), select the SpecQuant\Test Data\ directory.

5. Click SpecQuant's File menu and select Exit. This will bring up a Save file dialog box. Navigate to the main SpecQuant directory, and click the Select Folder button. SpecQuant should exit and a new file, "sqsettings.mat," will be saved in this directory. The settings file contains directory information that will be used in latter steps of the configuration process.

6. Run SpecQuant again. To perform quantitative analyses, SpecQuant needs to access standard library spectra (i.e., quantitative, pure-component spectra). SpecQuant was designed to work primarily with libraries of spectra that are stored on a computer using a simple directory structure like that used by the Northwest Infrared Gas-Phase Spectral Database[1,2] This structure consists of a root directory with subdirectories for each compound in the library. Multiple spectra of the compound can exist in a compound's directory (e.g., spectra of the compound measured at different temperatures). Furthermore, the spectral files can be in Galactic (.spc) or text (.txt) format. Here is a hypothetical example of a spectral library directory structure that could be used by SpecQuant:

```
[My BTEX Library] (root directory)
    [Benzene] (subdirectory with spectral files for benzene; e.g., benzene_25C.spc, benzene_50C.spc)
    [Toluene] (subdir with spectral files for toluene)
    [Ethylbenzene] (subdir for ethylbenzene spectra)
    [Xylenes] (subdir for xylene spectra)
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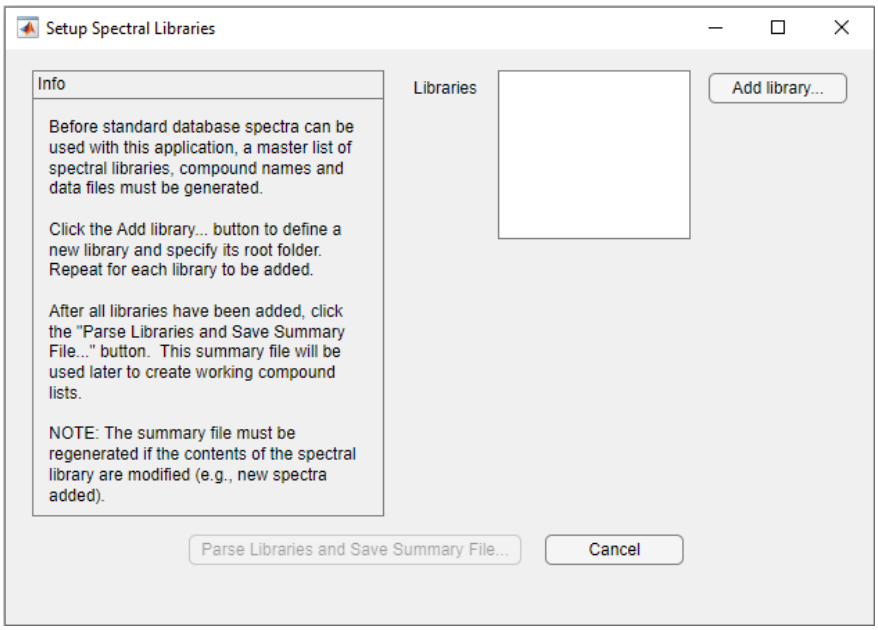
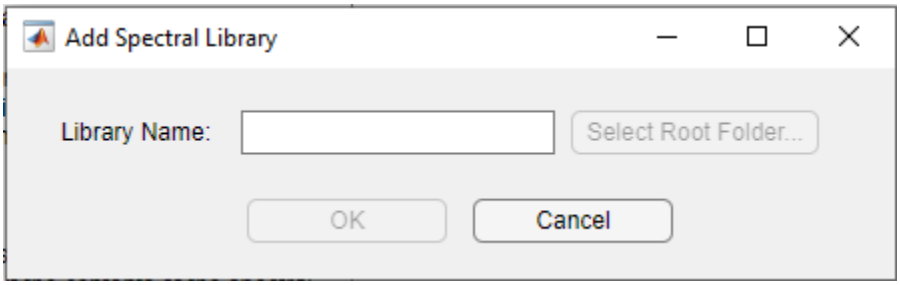
   SpecQuant is designed to parse this type of directory structure to obtain the names of compounds (subdirectory folder names) and the spectral data files available for each compound. Having SpecQuant "setup" a spectral library in this manner makes it easy to create working lists of compounds to include in a quantitative analysis task.

   The SpecQuant distribution includes a very small library of simulated spectra that can be used to test the software. Use the following steps to set up the test library—the same process can be used with other spectral libraries that have the directory structure described above.

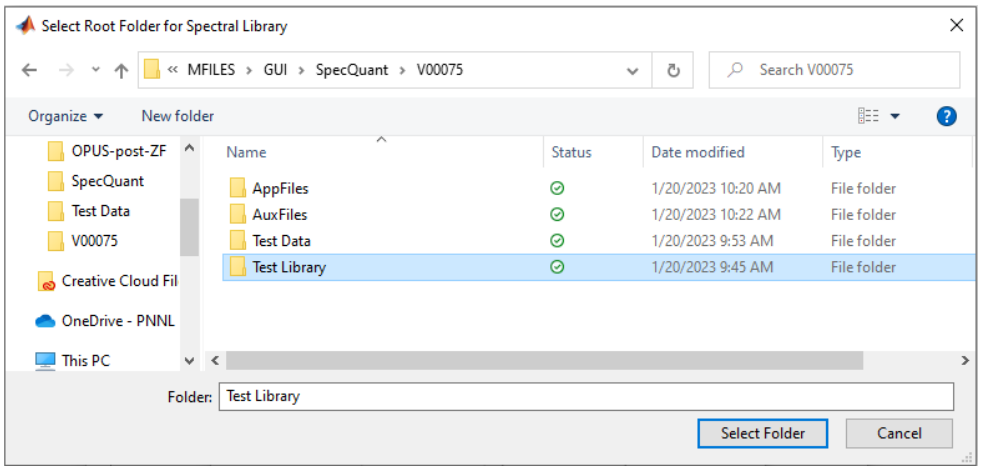
   a. Click SpecQuant's Tools menu and select "Set up Spectral Libraries…" This will bring up the following dialog box.



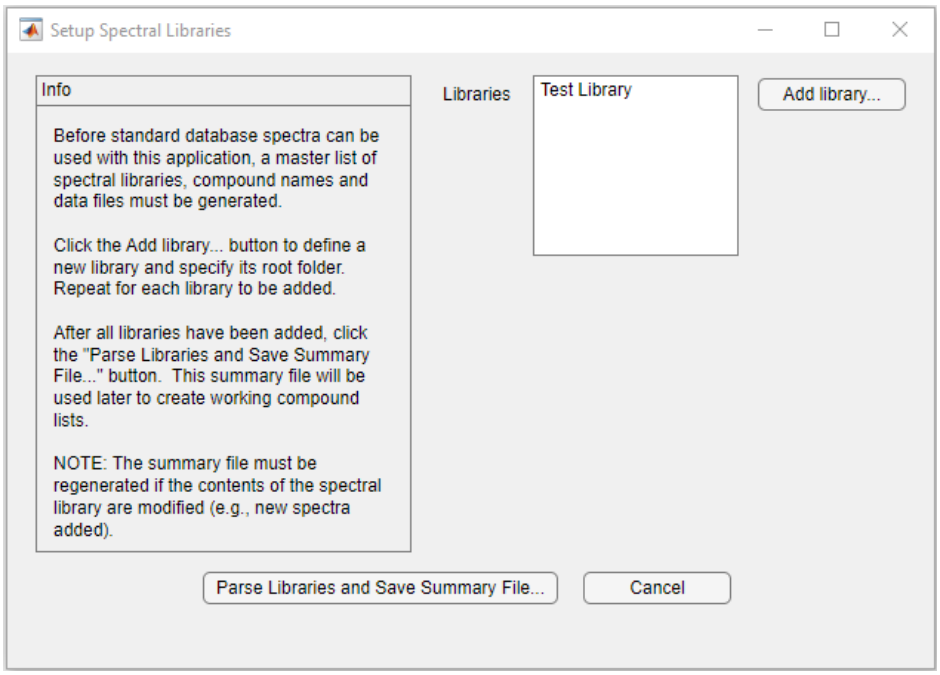
b. Click the "Add library…" button. This will bring up another dialog box:



c. Enter a name for the spectral library (e.g., Test Library) and click the "Select Root Folder…" button. Another dialog will prompt you for the folder. Navigate to the SpecQuant folder, select the Test Library folder, and click the Select Folder button.



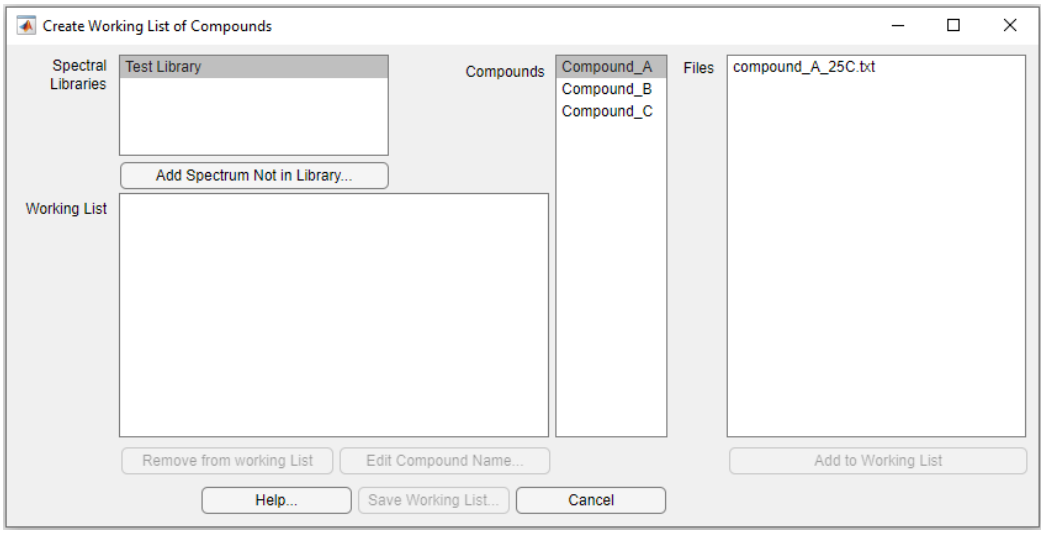
d. Click the OK button on the "Add Spectral Library" Dialog box. The Setup Spectral Libraries dialog should now include an entry for the Test Library.



e. Click the "Parse Libraries and Save Summary File…" button. When prompted, enter a name for the library summary file (e.g., "TestLibrarySummary.mat") and click the Save button. Note: It is recommended that you save this file in the main SpecQuant directory. You should see a message box indicating that the spectral library summary file was updated.

7. Set up a working list of database compounds using the following steps.

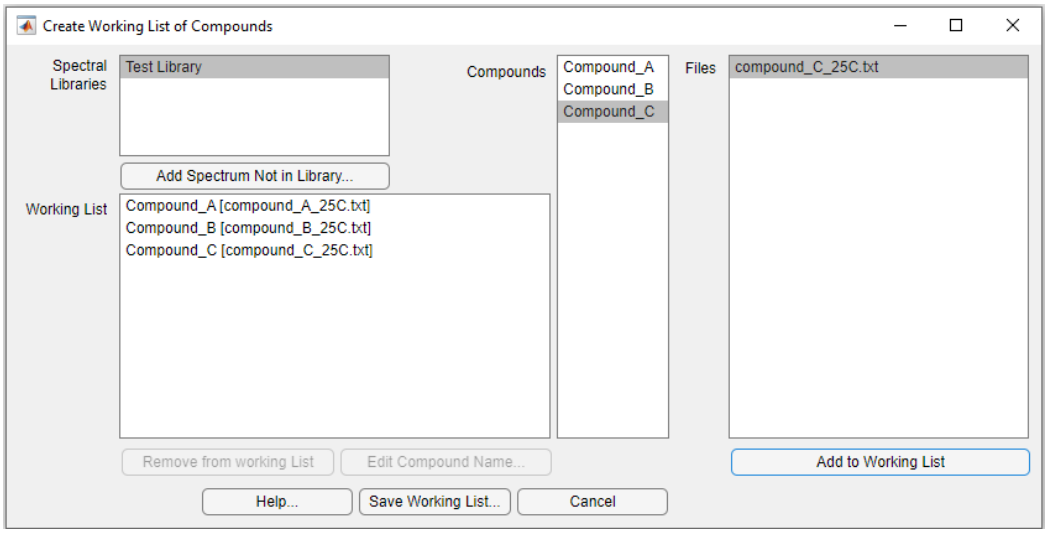
a. Click SpecQuant's Tools menu and select "Create Working List of Compounds…" This will bring up the following dialog box.



b. There are 3 compounds in the test database, and we will add all three of them to our working list. In the list of files on the right, select the single data file (compound_A_25C.txt), and click the "Add to Working List" button. This will add the

name of the compound and its file name to the Working List box on the left side of the dialog box.

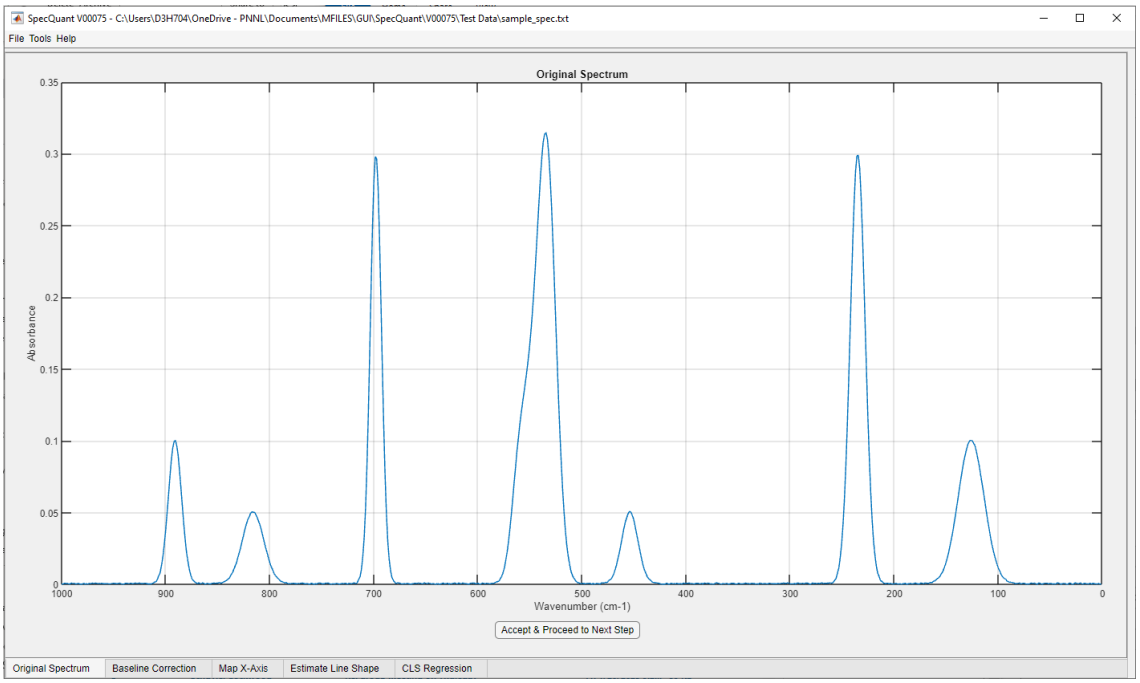
c. In the list of Compounds, select Compound_B, and then click the "Add to Working List" button again to add Compound B and its file to the working list. Repeat this process for compound C. The dialog box should now look like this:



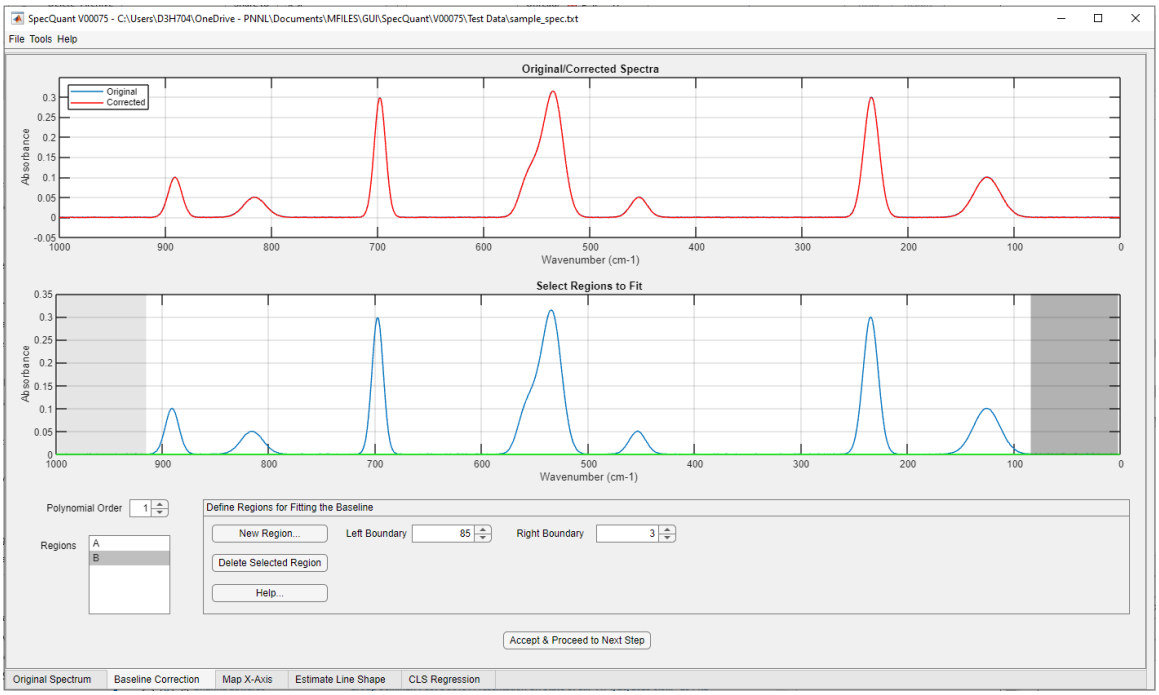
d. Click the "Save Working List…" button, and when prompted, enter a file name for the working list (e.g., "WorkingList_SimulatedData.mat") and click the Save button to save the file.

Performing Quantitative Analysis

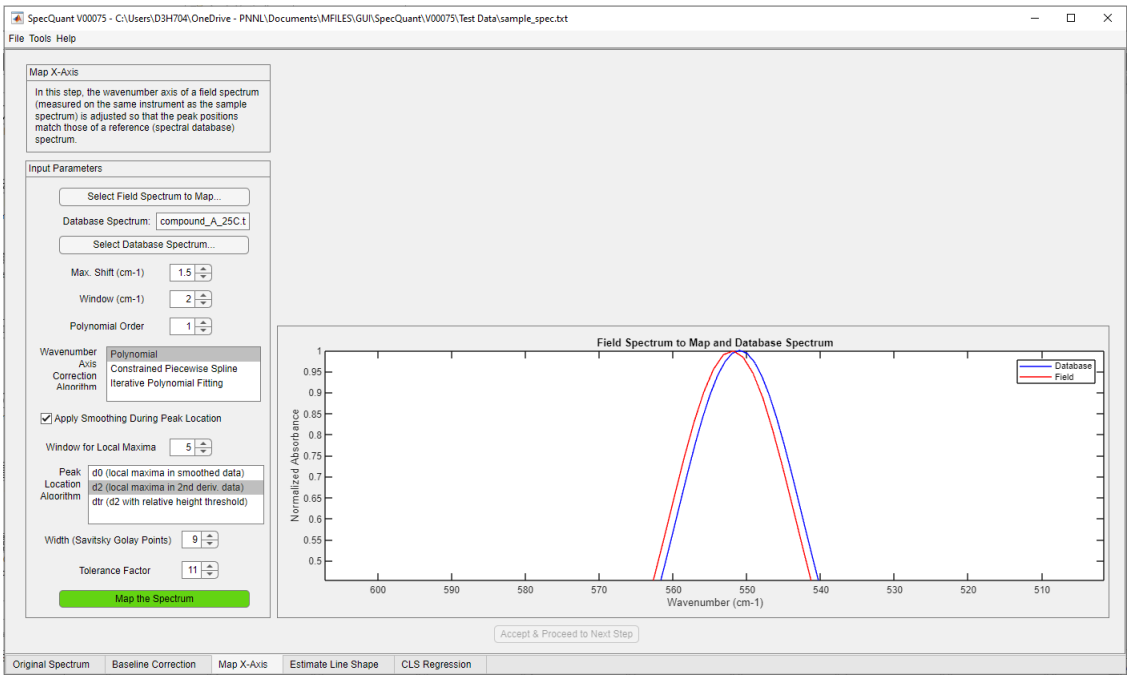
1. Click SpecQuant's File menu, select Open…, and navigate to the SpecQuant\Test Data\ directory. Select the file "sample_spec.txt" and click the Open button. SpecQuant should display a plot of the sample spectrum. In this example, the sample spectrum is a mixture of compounds A, B, and C; the respective concentrations are 0.1, 0.3, and 0.05 ppm. Note: SpecQuant can work with Bruker OPUS files, Galactic files (.spc), and text files (.csv and .txt).



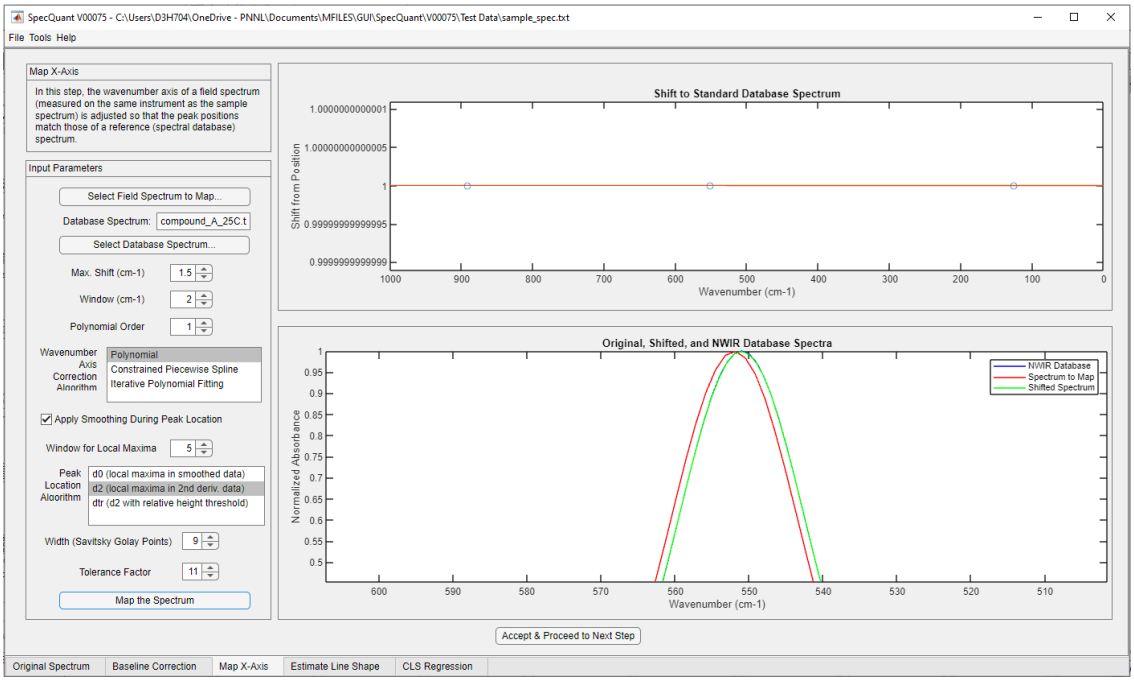
2. Click the “Accept & Proceed to Next Step Button”. This will bring up the Baseline Correction page. Baseline correction is not necessary for this test spectrum, but the process is demonstrated for reference. Baselines are corrected by selecting spectral regions that are free of absorbance features. A polynomial is then fit to the selected regions and is subtracted from the spectrum. Click the green “New Region…” button. The mouse pointer will change to a crosshair pattern. Click twice on the lower graph: first near the lower left corner of the plot and then again before the first peak (~930 cm-1). The wavenumber region will now be shaded gray. If desired, you can adjust the left and right boundaries of the region using the edit controls on the page. Click the “New Region…” button again and define another region by clicking just to the right of the rightmost peak (~90 cm-1) and again near the bottom-right corner of the plot. The display should look like the following. Click the “Accept and Proceed to Next Step” button to bring up the Map X-Axis page.



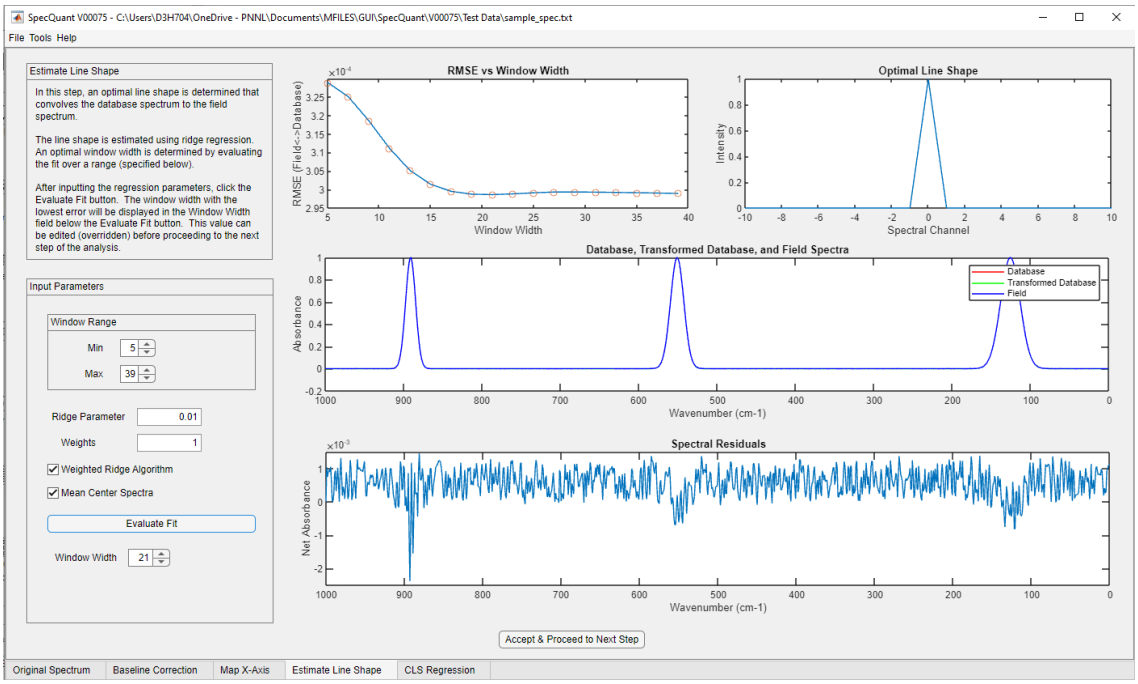
3. In this step, the wavelength axis of a "field" spectrum is aligned to that of a database spectrum. In a real scenario, the field spectrum could be a spectrum of water vapor that was measured on the same instrument used to measure the sample spectrum, and you would be aligning the wavelength axis to that of a database spectrum of water. For this example, we will perform our alignment using a slightly offset spectrum of Compound A. Click the "Select Database Spectrum…" button. When prompted for a file, navigate to the SpecQuant\Test Library\Compound_A directory, select the "compound_A_25C.txt" file, and click the Open button. Click the green "Select Field Spectrum to Map…" button. When prompted for a file, navigate to the SpecQuant\Test Data directory, select the "field_spec_A.txt" file, and click the Open button. Click and drag in the graph to zoom in on one of the peaks—the field spectrum's peaks are shifted to the left by 1 wavenumber relative to the database spectrum.



4. Click the “Map the Spectrum” button. A new plot will appear in the upper portion of the window that shows circles for the peaks that were detected. The y-axis of this plot indicates how much the peaks were shifted (all three peaks were shifted by +1 cm-1 in this example).



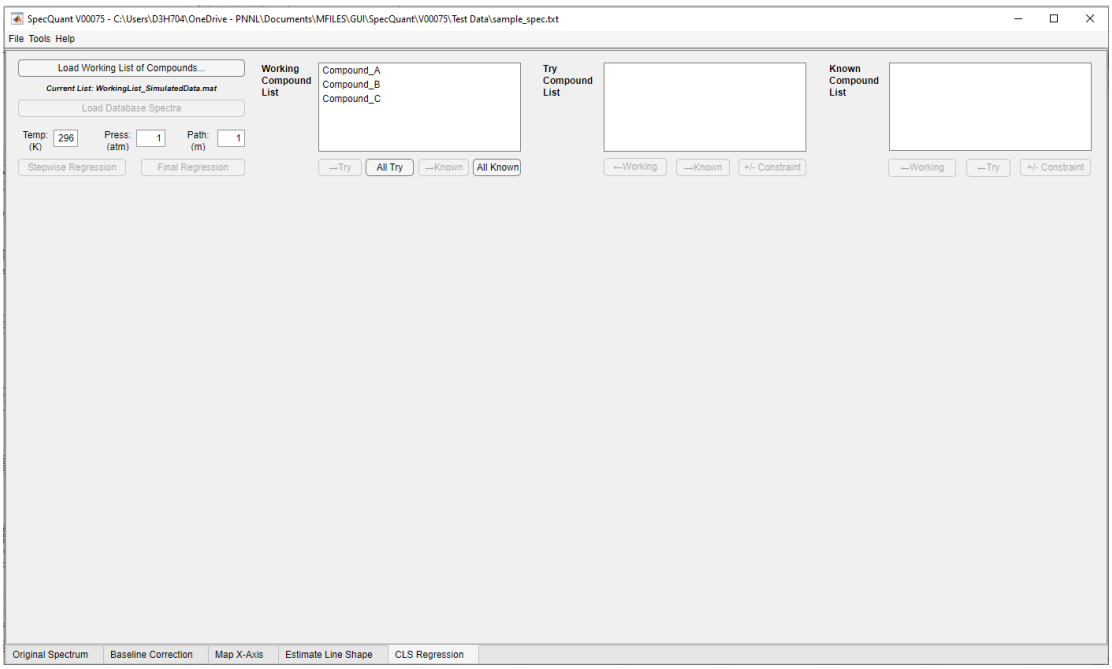
5. Click the “Accept & Proceed to Next Step” button to bring up the Estimate Line Shape page. Click the green “Evaluate Fit” button to determine the optimal line shape that convolves the database spectrum to the field spectrum.



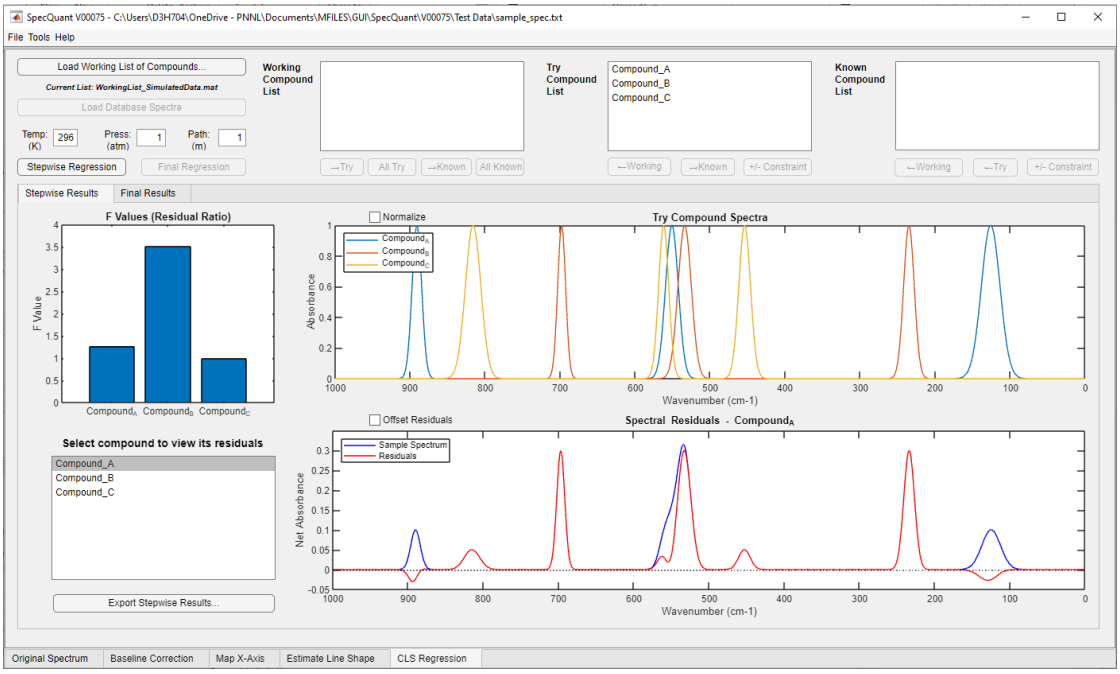
6. Click the “Accept & Proceed to Next Step” button to display the CLS Regression page.

7. The process for performing stepwise CLS regression using SpecQuant is described in detail in the accompanying journal article; only a brief description is provided here.

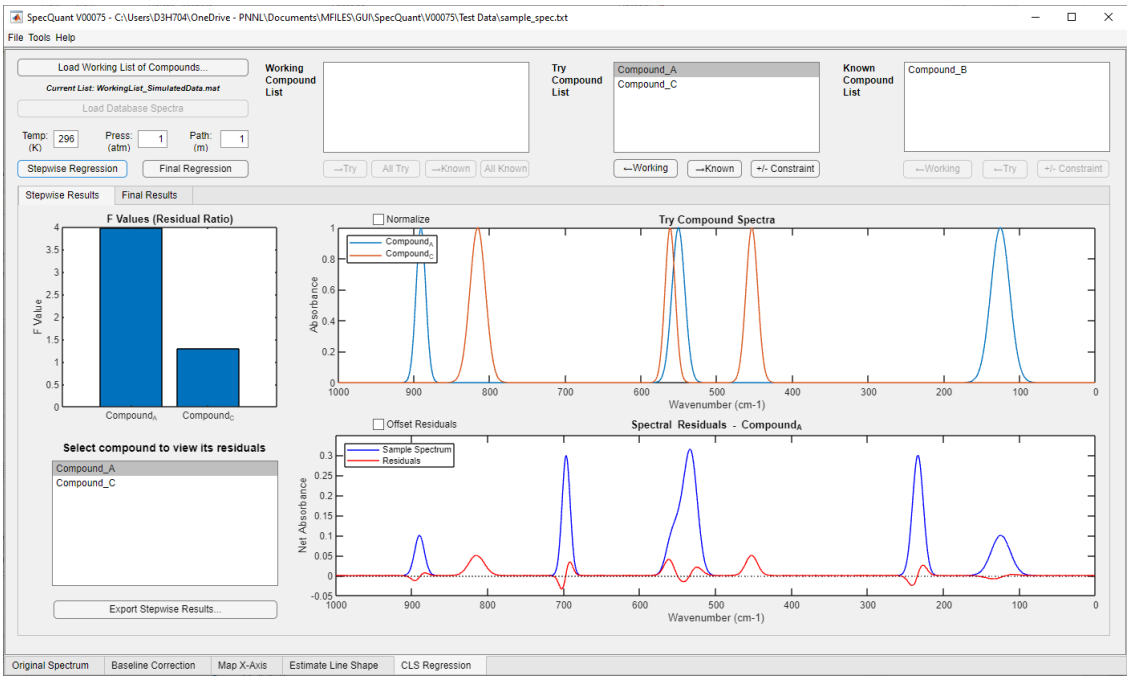
   Near the top left of the page, under the “Load Working List of Compounds…” button, the name of the current working list of compounds is displayed. This should be the name of the working list that was created in step 7d of the Installation and Configuration instructions. If another working list has been created, it can be loaded by clicking the “Load Working List of Compounds…” button. Once the name of the desired working list is displayed, click the green “Load Database Spectra” button. This loads the database spectra into MATLAB, interpolates their wavelength indices to match those of the sample spectrum, and deconvolves the database spectra using the line shape that was estimated previously. A popup message indicates the database spectra have been loaded.



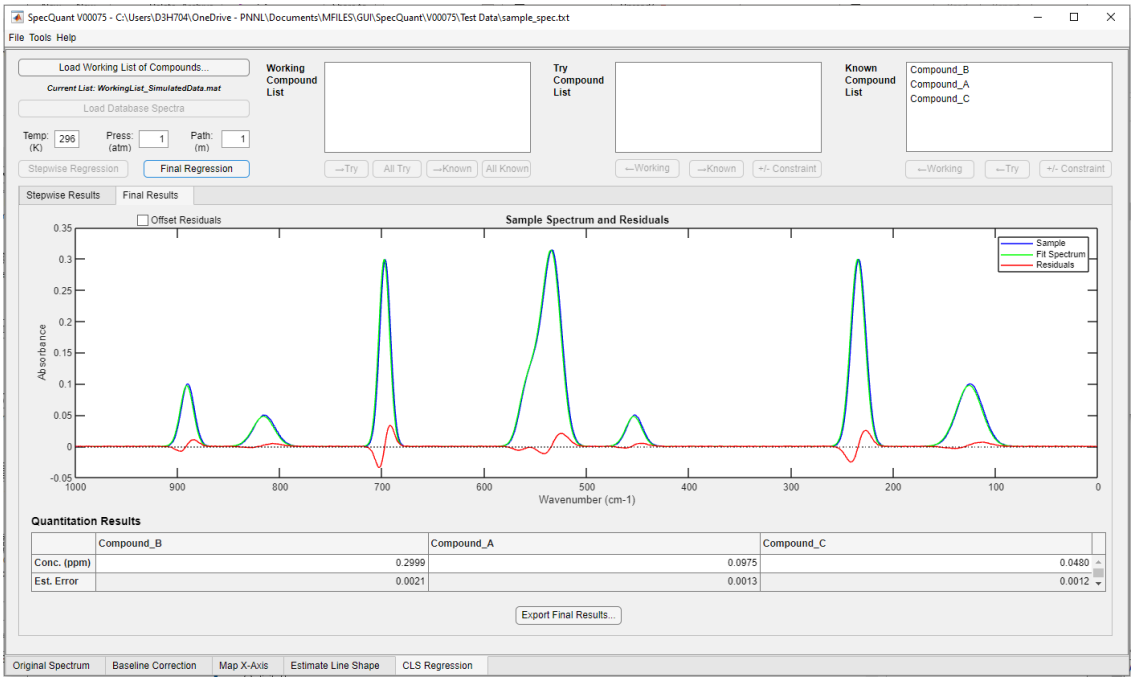
Click the “All Try” button to move all 3 compounds into the Try Compound List. Next, click the “Stepwise Regression” button near the left side of the page. This shows the initial fitting results. Note that compound B has the highest F-value (bar graph) with a value of ~3.5, which makes compound B a good candidate to add to the Known Compound List.



Click on Compound_B in the Try Compound List and then click the “→Known” button below the Try Compound List box. This will move Compound_B to the Known Compound List. Click the “Stepwise Regression” button to perform the next step of the analysis.



Add compounds B and C to the Known Compound List and click the “Final Regression” button.



This shows the “final” fit and estimated mixing ratios. The quantitative estimates for compounds A, B, and C agree well with the true values of 0.3, 0.1, and 0.05 ppm. Results from the analysis can be exported to a MATLAB file by clicking the “Export Final Results…” button.

References

1. Sharpe, S.W., T.J. Johnson, R.L. Sams, P.M. Chu, G.C. Rhoderick, and P.A. Johnson. 2004. “Gas-Phase Databases for Quantitative Infrared Spectroscopy.” *Appl. Spectrosc.*, *58*, 1452-1461.

2. Brauer C.S., T.J. Johnson, T.A. Blake, S.W. Sharpe, R.L. Sams, and R.G. Tonkyn. 2014. “The Northwest Infrared (NWIR) gas-phase spectral database of industrial and environmental chemicals: Recent updates.” In *Advanced Environmental, Chemical, and Biological Sensing Technologies XI, May 5, 2014, Baltimore, Maryland. Proceedings of the SPIE*, edited by T Vo-Dinh, RA Lieberman and GG Gauglitz, 9106, Paper No. 910604. Bellingham, Washington:SPIE. PNNL-SA-102648. doi:10.1117/12.2053591