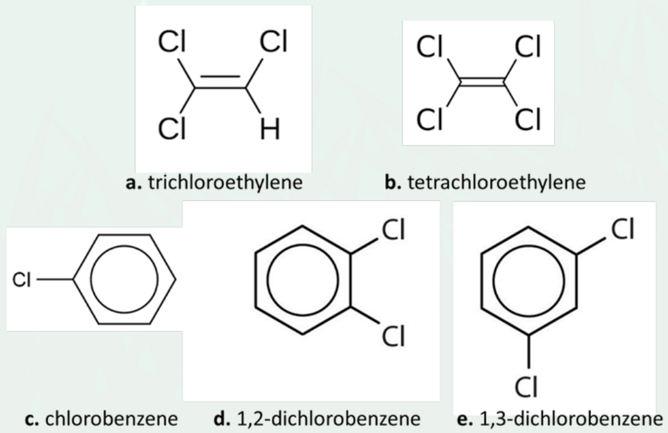
Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) Detection of Chlorinated Hydrocarbons in Groundwater

Presented by Dr. Randall D Maples

Chlorinated Hydrocarbons

- Chlorinated hydrocarbons including aliphatic and aromatic compounds (CHCs) are toxic contaminants commonly found in groundwater samples and efficient detection and monitoring of these contaminants is an important part of the evaluation of water quality.

- The detection of CHCs in the aqueous environment is often accomplished through the use of chromatographic and spectroscopic techniques such as high-performance liquid chromatography (HPLC), gas chromatography and mass spectrometry (GC-MS), ultraviolet (UV), visible (VIS), infrared (IR) or Raman spectroscopy. Analysis is often complicated due to the presence of many compounds as well as interfering molecules.

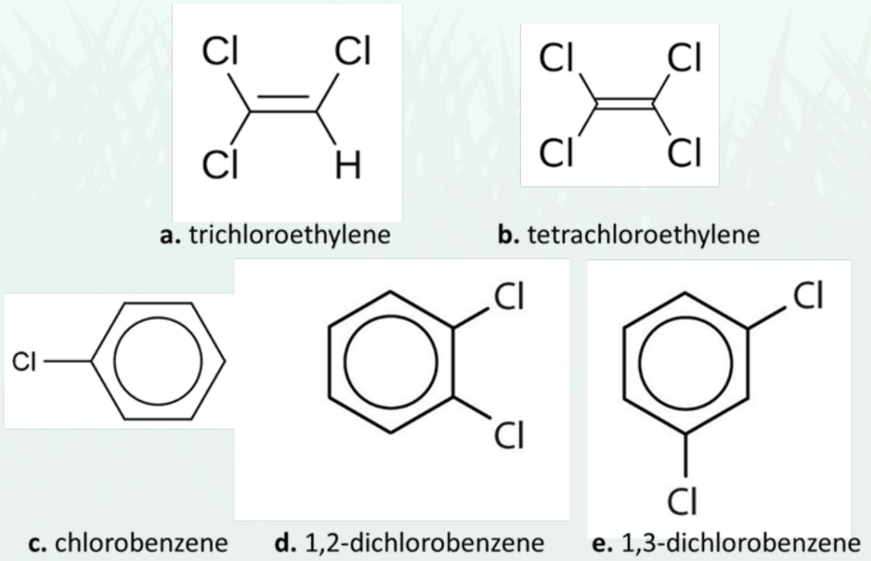


a. trichloroethylene **b.** tetrachloroethylene

c. chlorobenzene **d.** 1,2-dichlorobenzene **e.** 1,3-dichlorobenzene

Chlorinated Hydrocarbons

- In this preliminary study, with an overall end-goal of the development of a novel, time and cost-efficient procedure for the determination of complex mixtures of CHCs in groundwater employing digital signal processing techniques, we intend to develop a method for the determination of various CHCs in aquifer groundwater using ATR-FTIR.



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Chlorinated Hydrocarbons

- Under aqueous conditions, small amounts of hydrocarbons are difficult to detect due to their low concentration in water and sensing of these types of compounds in an aqueous environment remains a challenging analytical task.

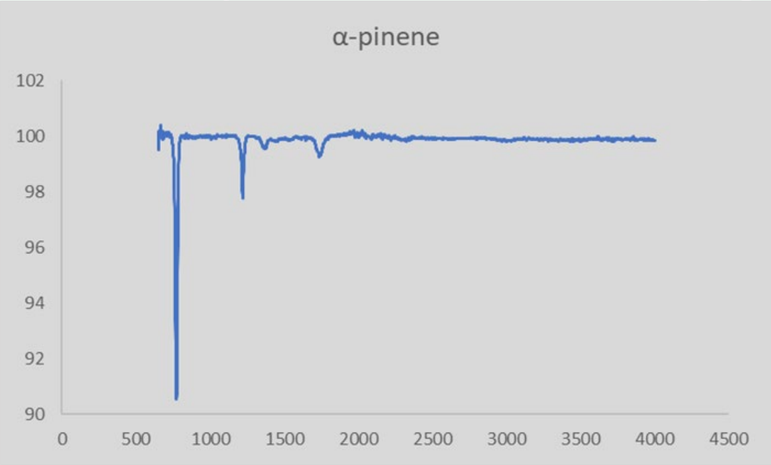
- Fourier transform infrared spectroscopy is known as a rapid and non-destructive detection technology for organic constituents due to the generated fingerprint spectra. Especially, the combined use of ATR with FTIR enables a direct examination of liquid phase samples without further preparation.

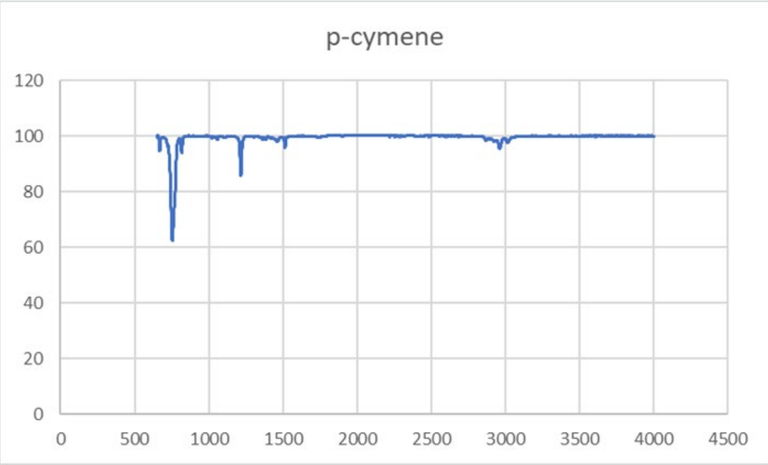
- Chemometric techniques have been applied in a wide array of chemical problems with huge successes in the acquisition of chemical data from an instrumentation followed by quantitative chemometric analysis using partial least squares (PLS) regression.

Analysis

- In order to obtain the needed data for chemometric quantitative analysis of CHCs, the method was first designed for the analysis of a non-aqueous mixture of compounds where extraction from water was not necessary, thus terpenes were selected to use.

In order to obtain the needed data for chemometric quantitative analysis of CHCs, the method was first designed for the analysis of a non-aqueous mixture of compounds where extraction from water was not necessary. Water exhibits a broad -OH peak whose wavenumber (cm^{-1}) will cover up a lot of other peaks that you are interested in.

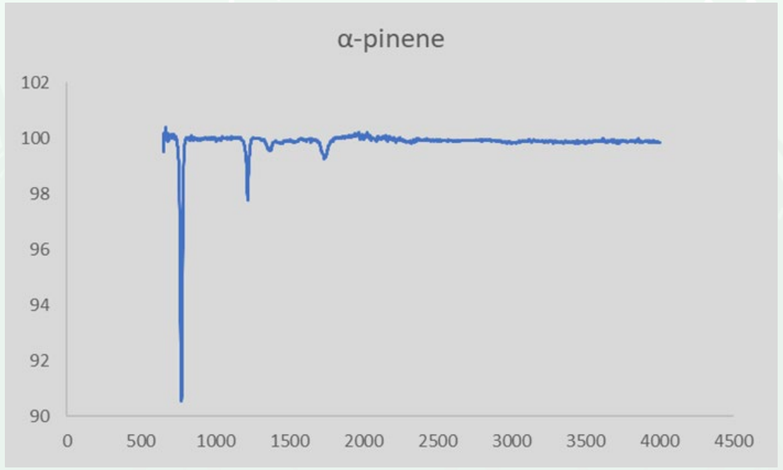


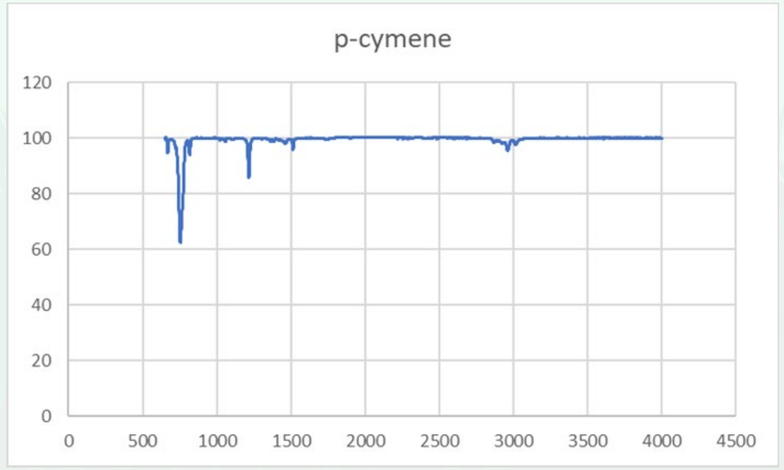


ATR-FTIR spectra of both pure and mixed terpenes were taken

Analysis

Each spectral measurement was thoroughly investigated by identifying peaks which differentiate one terpene or CHC unique from the other.





The IR spectra of each terpene and CHC is characterized by specific cm^{-1} corresponding to a specific functional group.

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Analysis

Figure 4. RStudio program was used for PLS regression and signal processing.

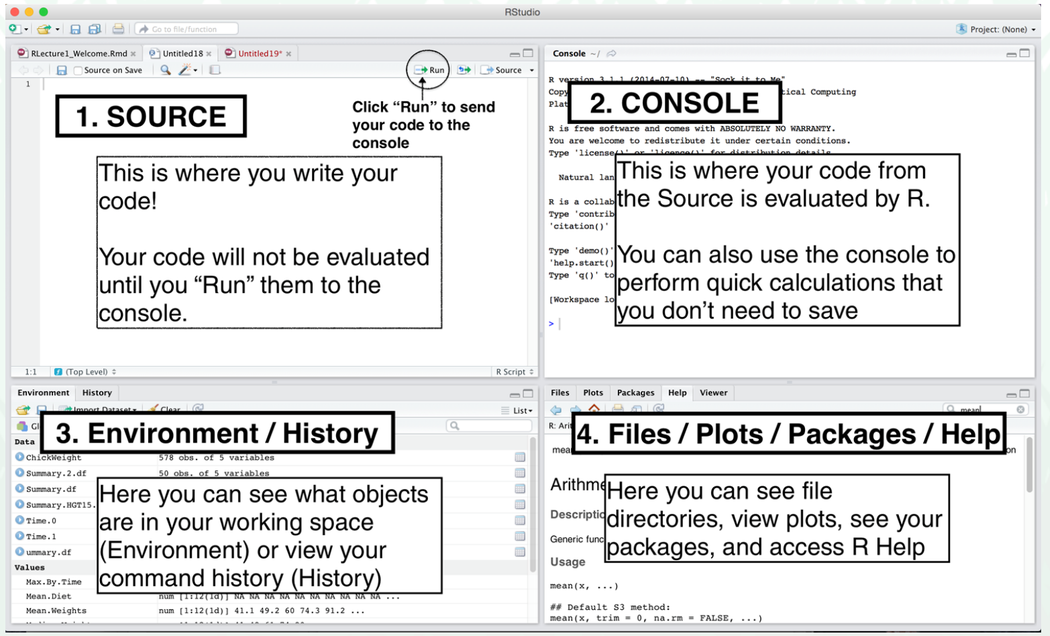

Figure 4. RStudio program was used for PLS regression and signal processing.

The process we used to for our experiments is described below:

- Prepare and obtain ATR-FTIR spectra of pure CHCs and mixtures of CHCs to identify unique spectral regions for each of the analytes.
- Use R Program (RStudio environment **Figure 4.**) for quantitative chemometric analysis of the mixtures using partial least squares (PLS) regression.

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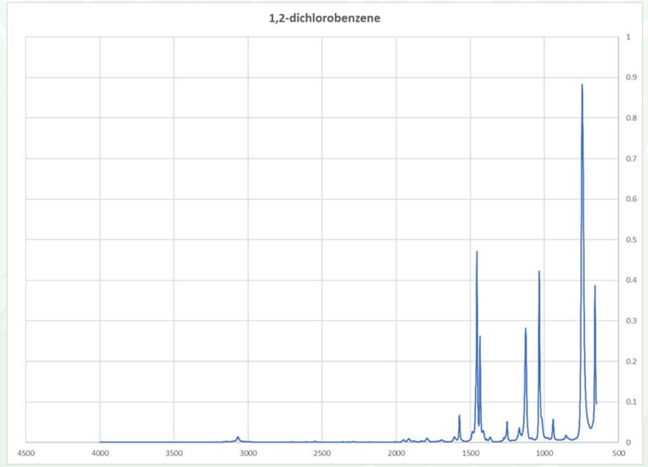
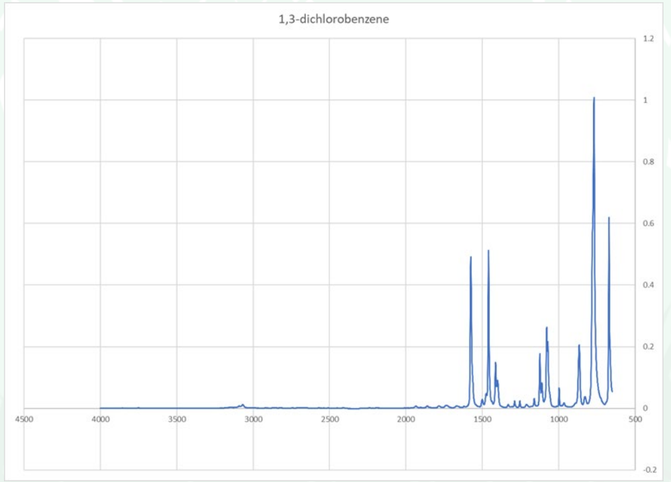
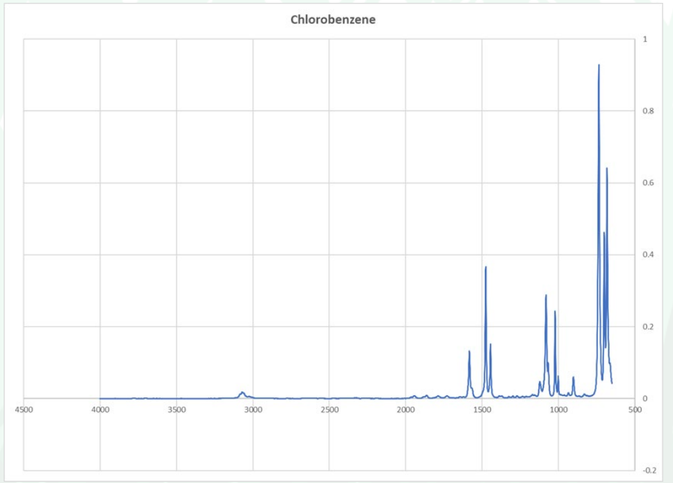
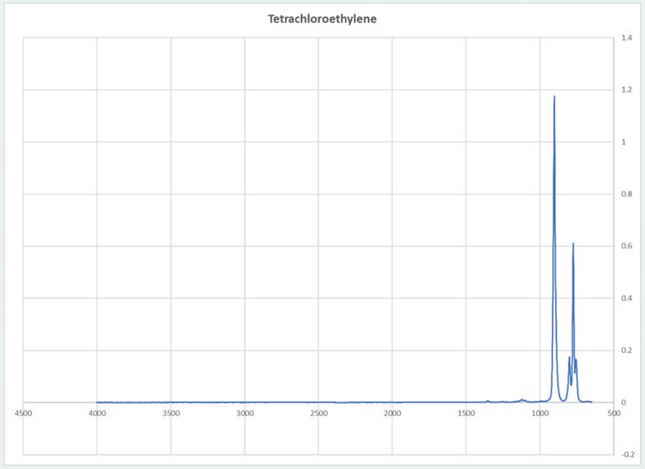
Results

- Each spectral measurement was thoroughly investigated by identifying peaks which differentiate which make one terpene or CHC unique from the other.

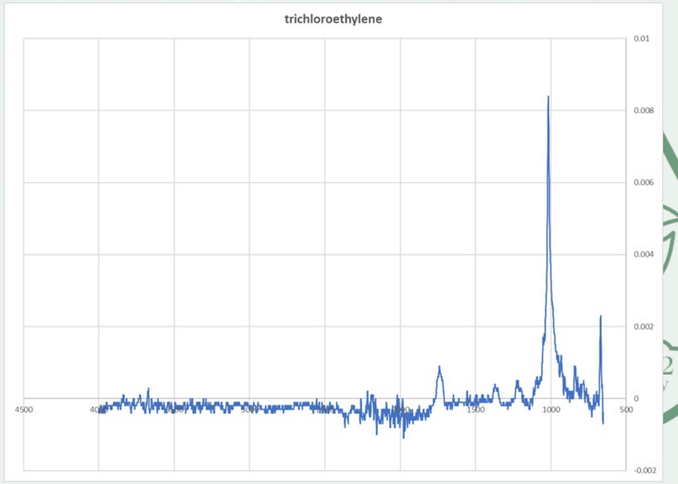






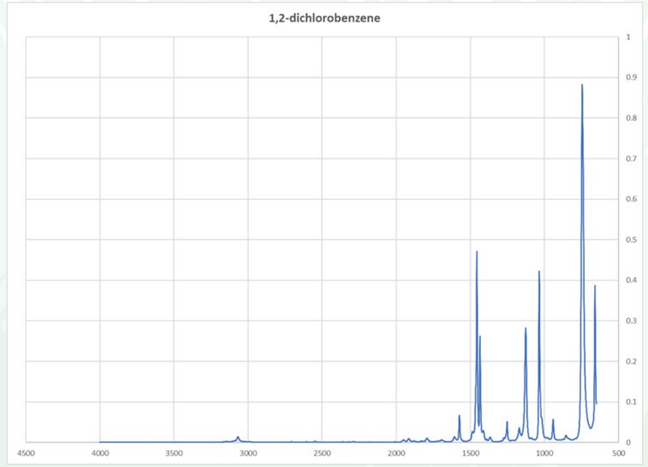


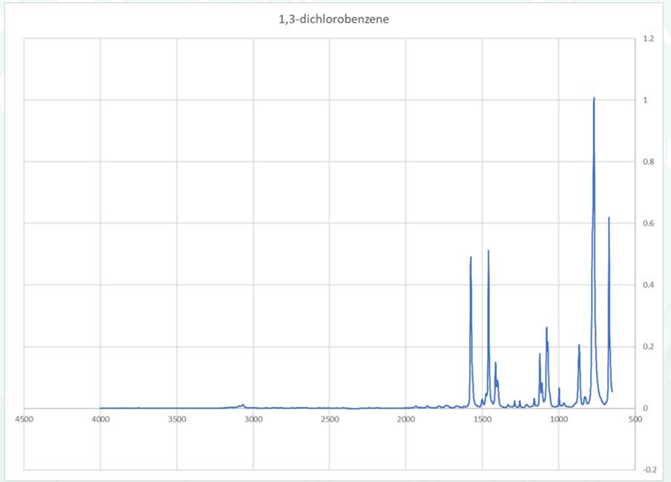
Figures: ATR-FTIR spectrum of CHCs

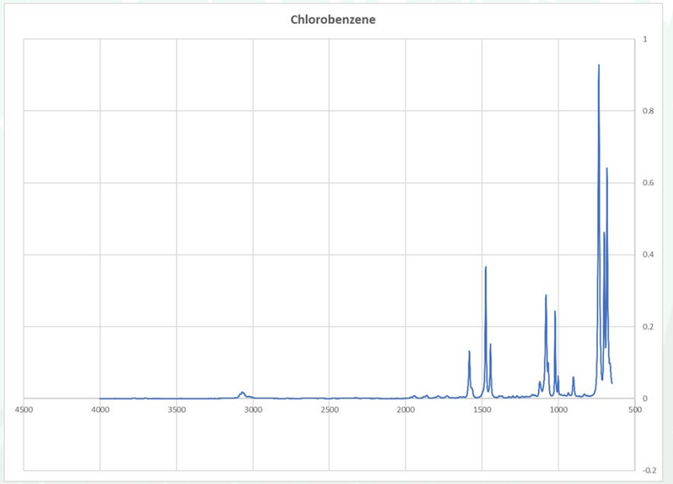


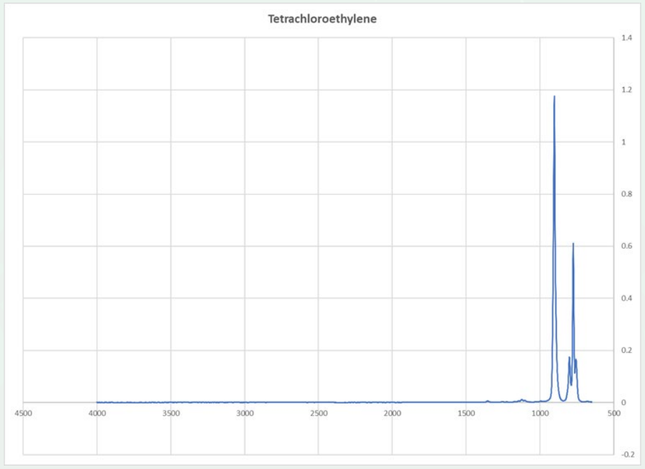
Results

The unique spectral differences among the pure terpenes and CHCs clearly indicate that subtle differences would be sufficient to distinguish one analyte from the other -- key elements which can be crucial to detect the presence of each.









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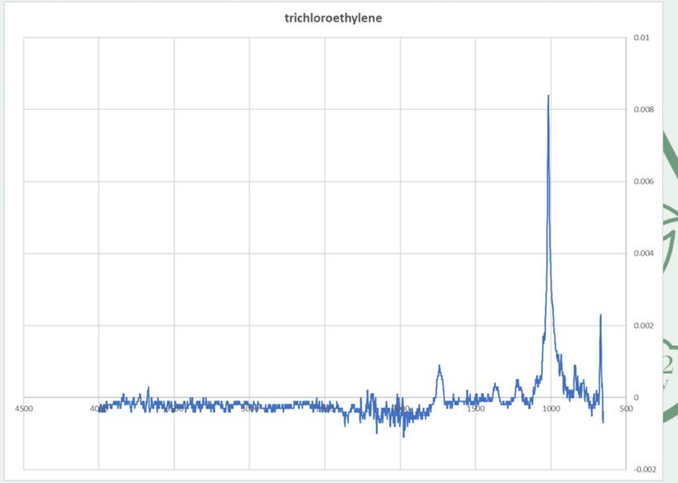
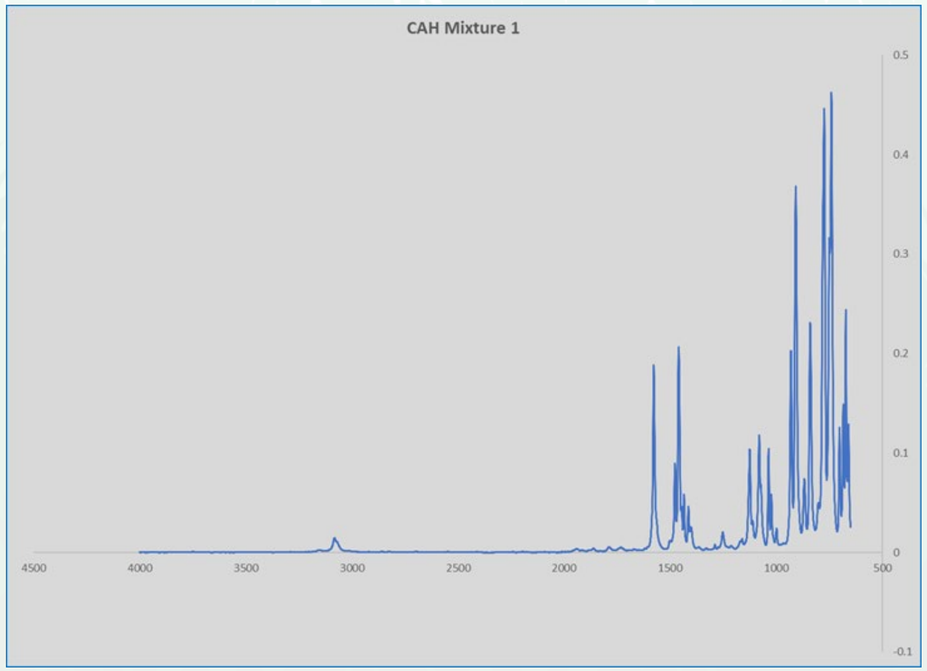


Results

- The identifying peaks were then used in the programming within the RStudio program for PLS regression and signal processing.
- This involved preprocessing acquired FTIR data followed by simultaneous quantitative determination of the prepared terpenes using PLS.



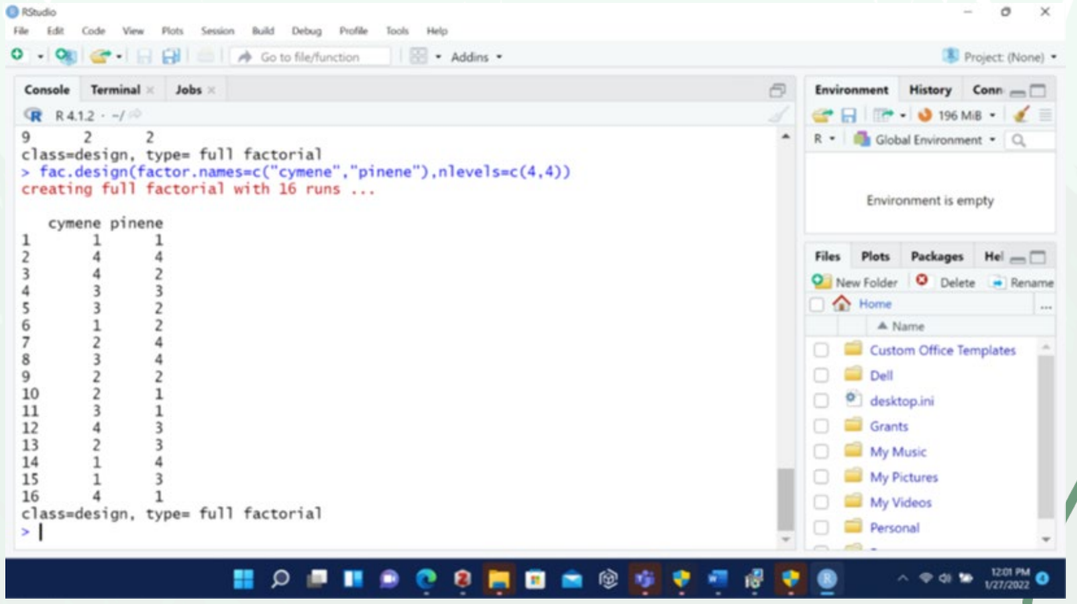


Figure 6. ATR-FTIR spectrum of CHC mixture

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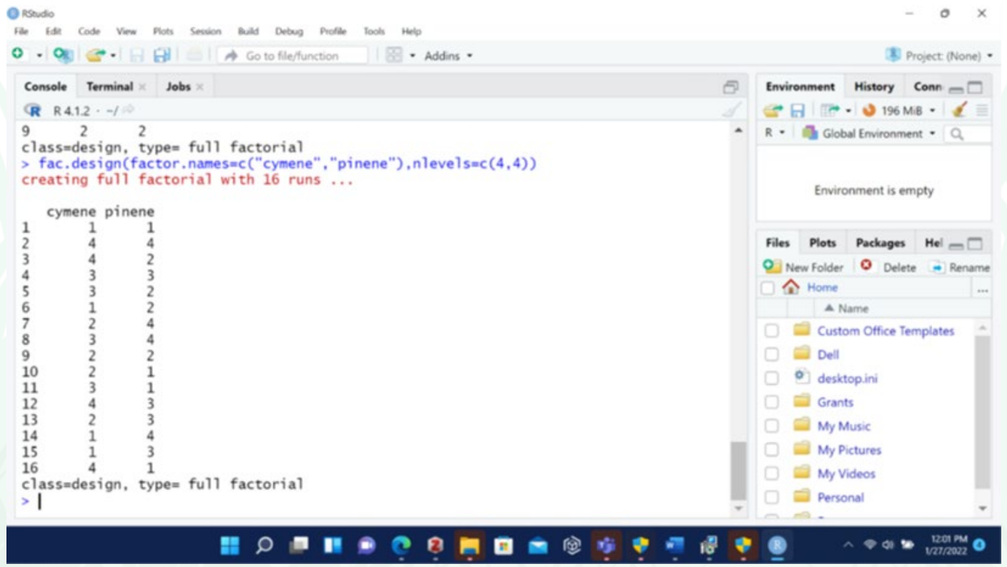
Results



Analysis of the designed set indicate that the developed predictive model generated appropriate detection components, which would be sufficient to develop a robust PLS model for determining the percent w/w of the components in the data set.

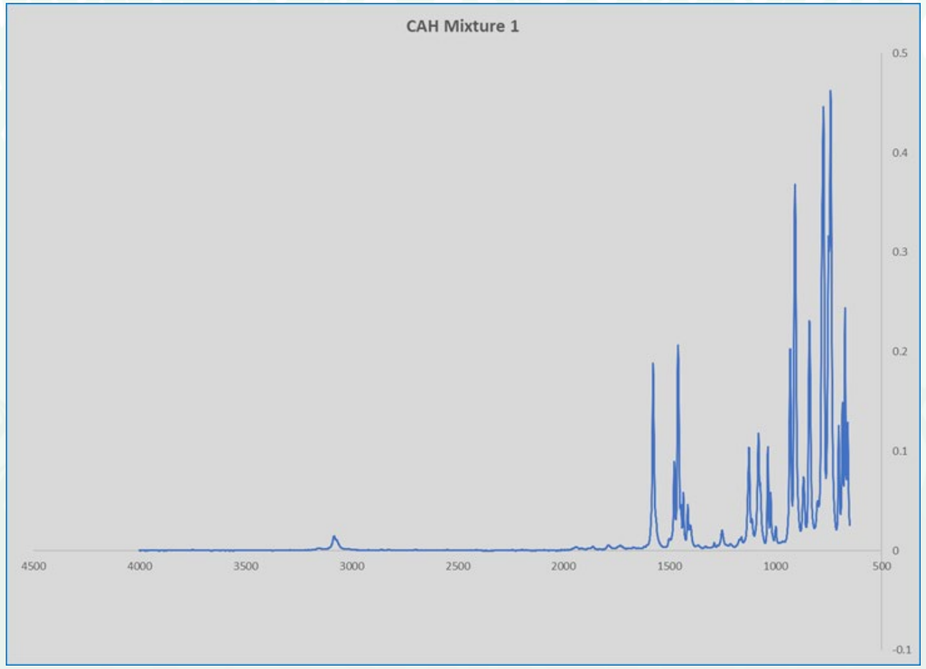


Figure 6. ATR-FTIR spectrum of CHC mixture

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Results

The results of the analysis show overall larger RMSE values for CHCs as compared to terpene samples. (**Figure 16**).

RMSE values provide you with an idea of how well the “fit” is in the mode.

The smaller the value the better.

Data Set	RMSE
Terpenes LC	12.11
Terpenes MC	9.61
Terpenes HC	4.54
CHC LC	21.34
CHC MC	18.25
CHC HC	16.47

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N} \left(y_i - y_i'\right)^2}{N}}$$

Figure 16. RMSE values for terpene and CHC data

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Results

The results of the analysis show overall larger RMSE values for CHCs as compared to terpene samples. (**Figure 16**).

Terpenes mixtures yielded better fits which is not surprising.

The model performed well in both analyses.

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Results

This indicates that, although the program performs very well, there is still room for improvement in CHC analysis.

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Results

During the next phase of our research, we will look at refining the unique spectral regions we are using to in the analyses of the mixtures

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Figure 16. RMSE values for terpene and CHC data

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Special Thanks

We would like to thank The Oka' Institute for this tremendous opportunity!

Thank you to undergraduate student Jarett A. Williams for his contributions in research and programming.

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