Reaction Monitoring with the ReactionView® System

Remspec Corporation

Remspec has been manufacturing and selling mid-IR fiber optic systems since 1993 (twenty years).

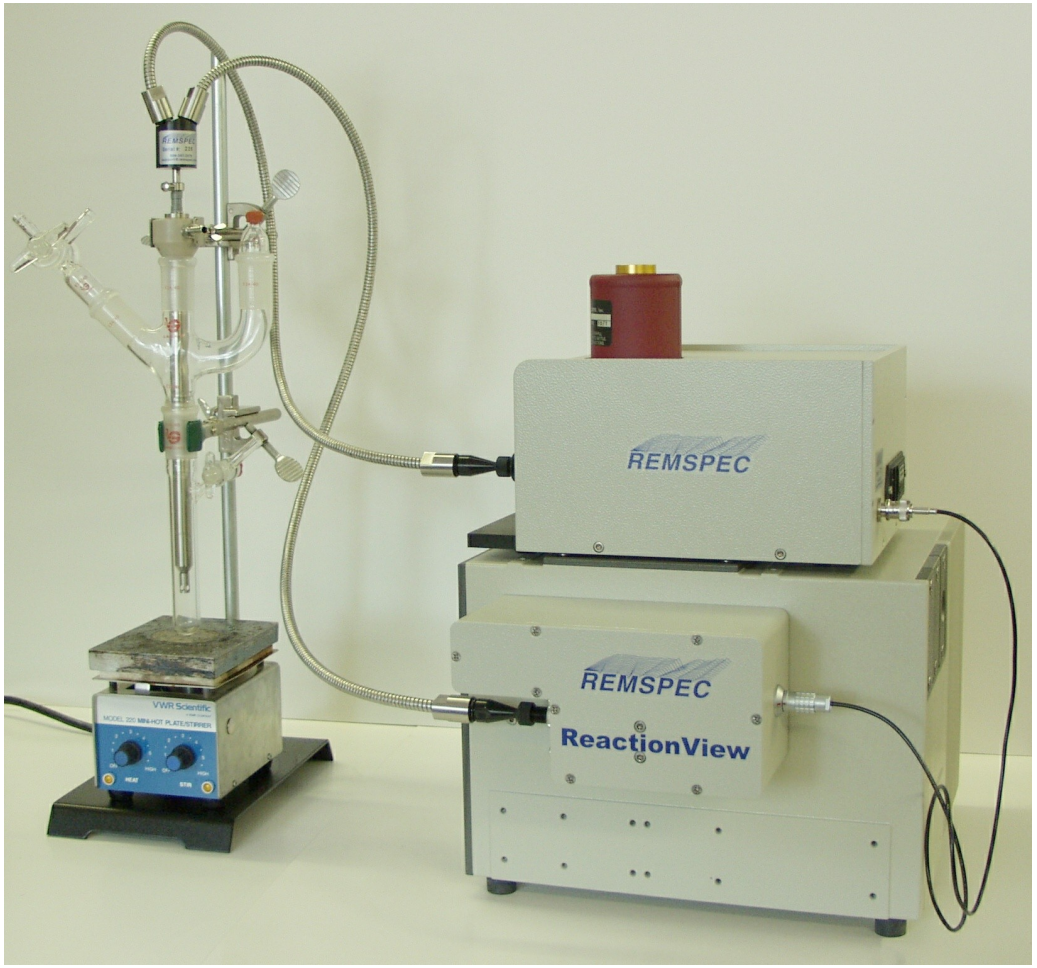
We have sold over 200 fiber-optic probes and systems to academic and industrial customers all over the world.

We have more experience with mid-IR fiber optics than any other company.

Our software is designed by synthetic chemists to be used by chemists, We can provide fully customized software.

Our experienced scientific staff provides full support for applications development.

ReactionView®



Range 900-5000 cm^{-1}

ATR and transmission heads fit wide range of reactors

Full control and display software on a laptop

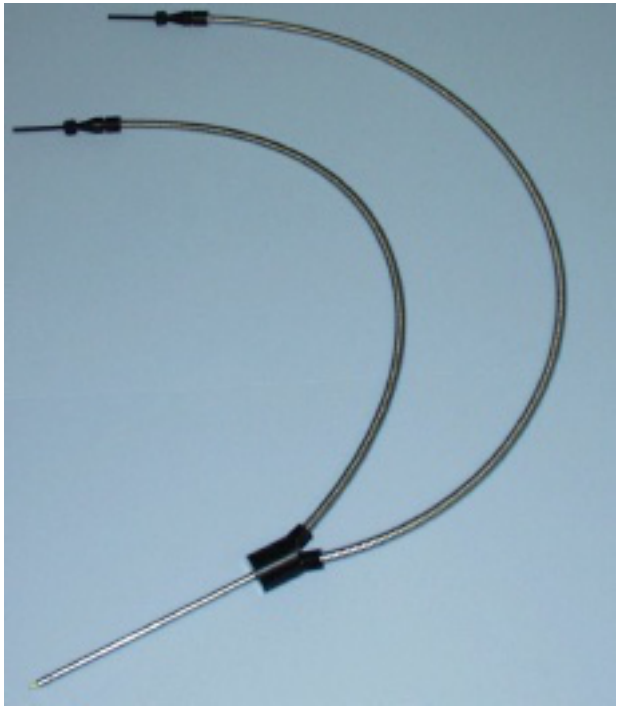
20 hr detector dewar for overnight experiments

Modular Systems

Remspec systems are fully modular

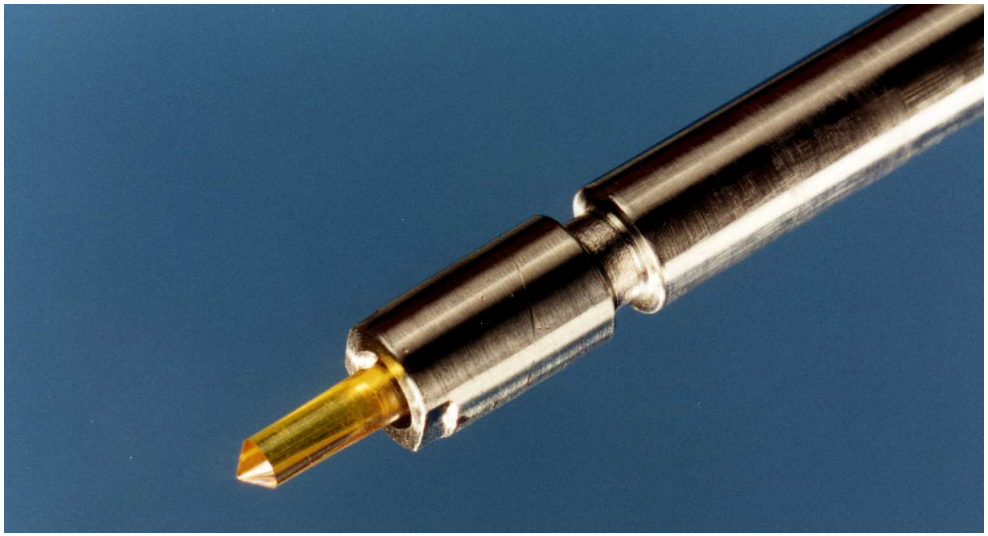
- Analysis heads for high or low temperature, high pressure, corrosive solvents
- Replaceable ATR crystals for standard conditions, high and low pH, corrosive conditions
- Liquid transmission head for very low concentrations
- Short-path gas transmission cell
- Only the head is changed for changing conditions or different types of reactor port

Mid-IR Probes with interchangeable heads



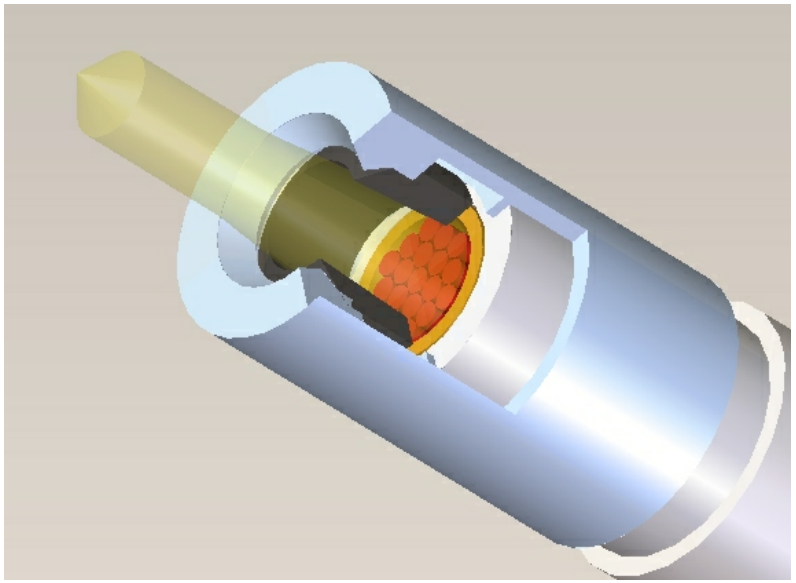
Fiber-optic probe with cables

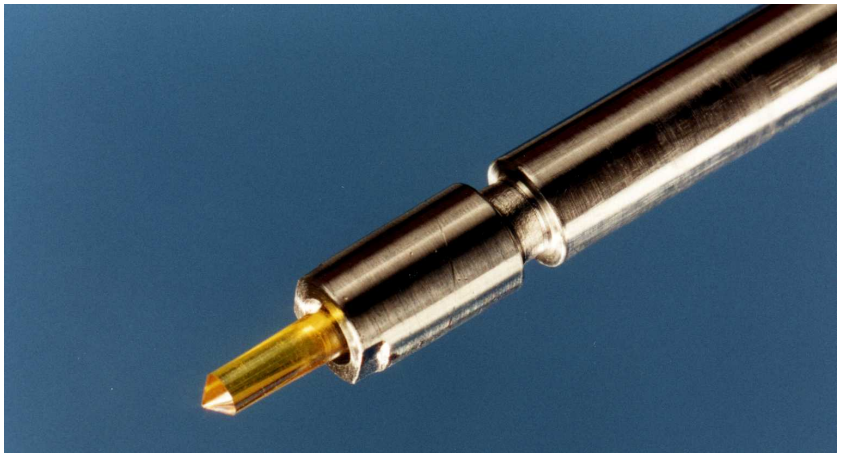
Liquid transmission head



ATR head (with ZnSe crystal)

ATR Head

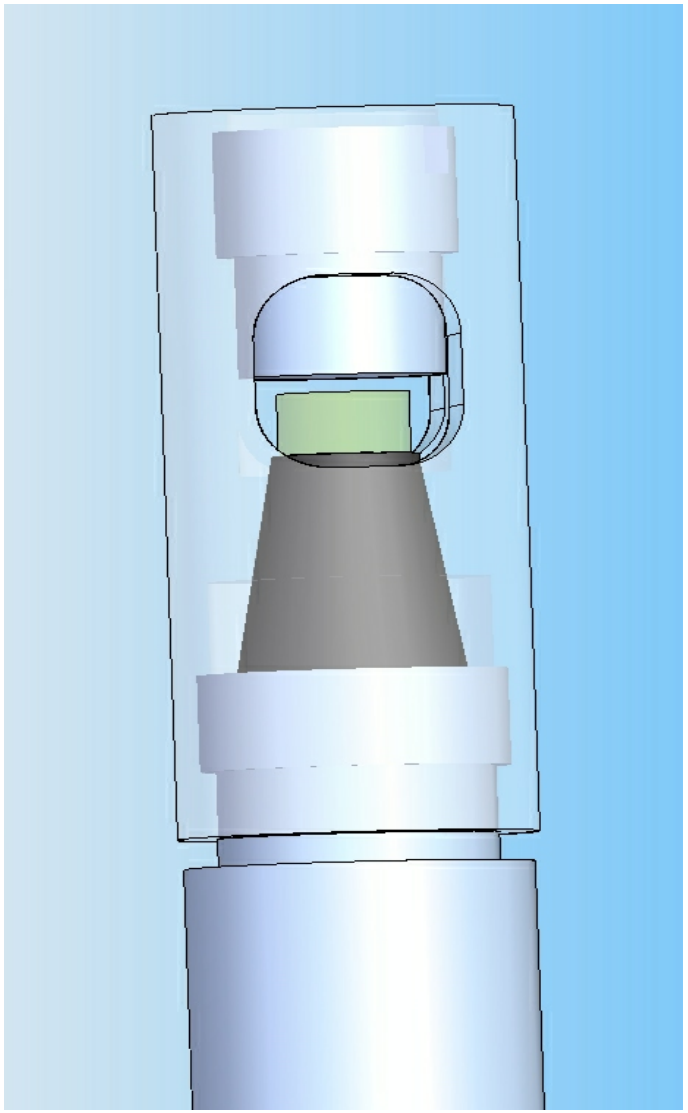




- A range of materials can be used (ZnSe is shown)
- Good, general-purpose probe
- Sensitive down to about 0.1 wt.% of most analytes
- Works in all solvents, including water
- Stainless steel* probe, shaft graphite-filled Teflon® seals, and inert crystal materials make the probe corrosion-resistant.

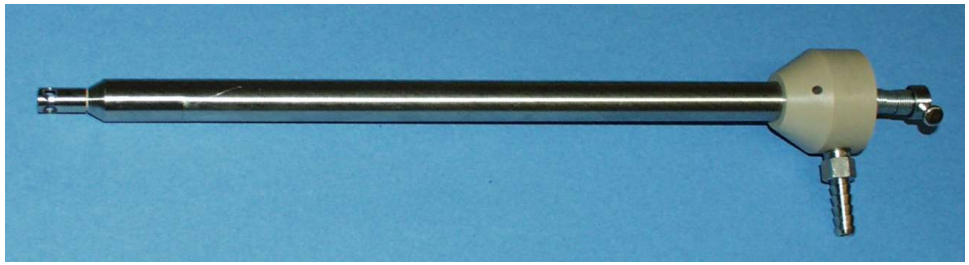
**Hastelloy is available for extreme conditions*

Transmission Head



- The Liquid Transmission Head lowers the detection limit to <0.1mM.
- It is a double-pass transmission cell with a mirror wall.
- It can only be used in solvents that have low mid-IR absorbance (e.g. hexane,acetonitrile, methylene chloride, THF); suspended solids can interfere with performance.

Analysis Heads: High Temperatures



High Temperature Head

Gas cooled (air or nitrogen)

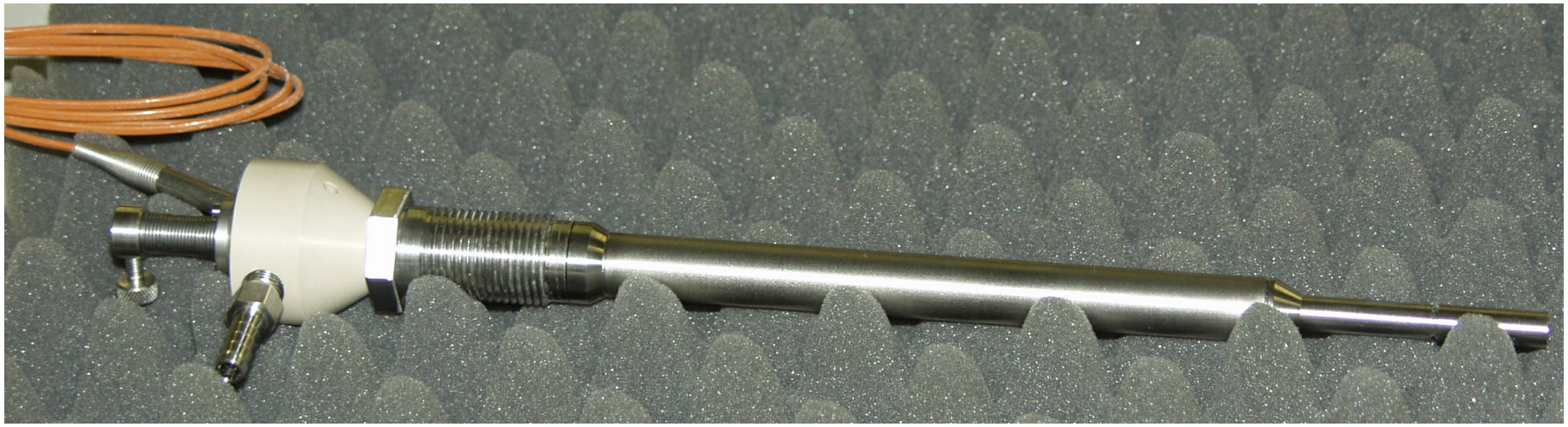
ATR or Transmission

-100ºC to >200ºC

15mm OD

Available with chemically resistant polymer end for low heat transfer

In-Situ Spectroscopy at High Pressures



High Pressure Head (example)

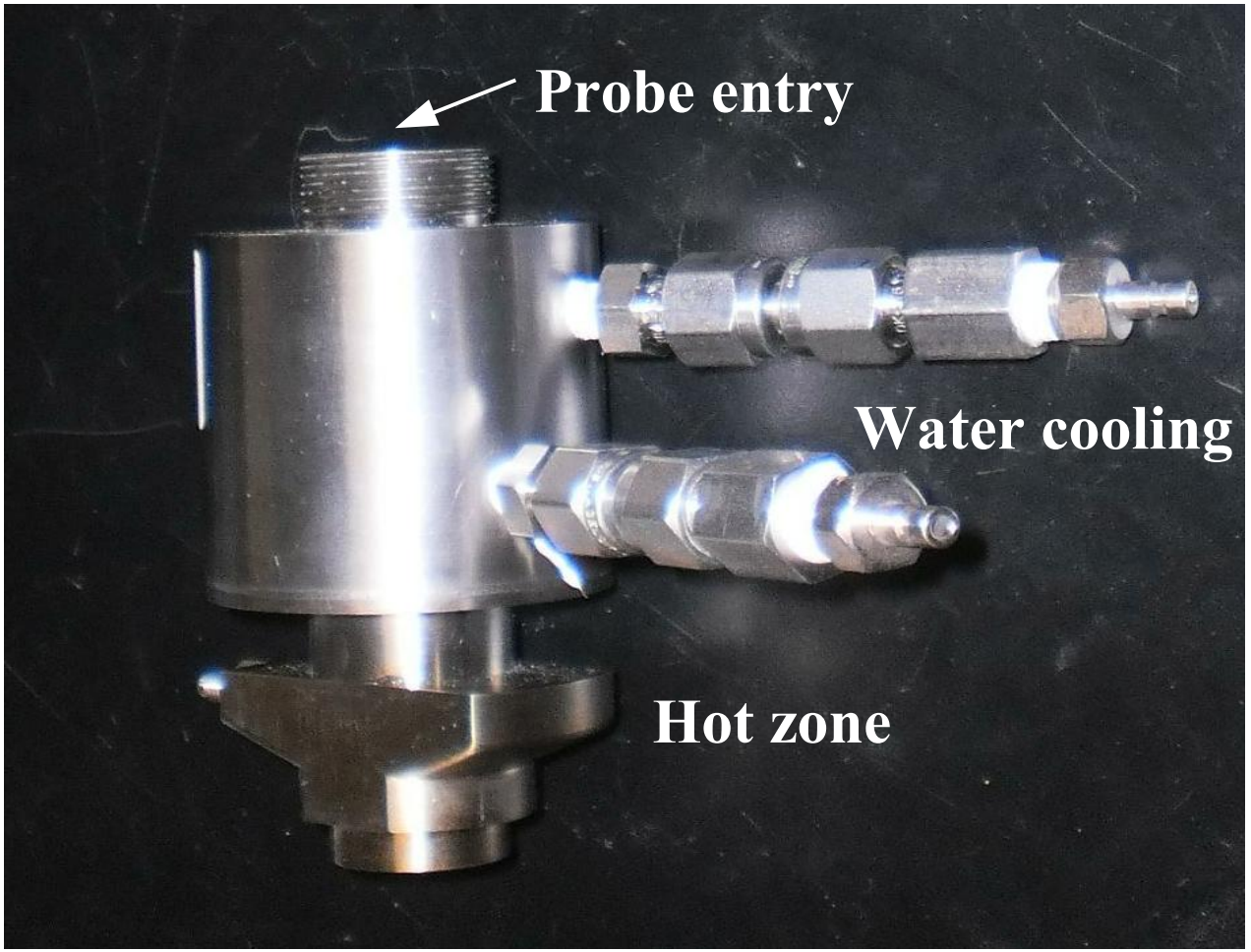
Custom HIP style (cone in cone fitting shown)

ATR or Transmission Pressure to >200 bar

Cooled (air or nitrogen), -100ºC to 300ºC (standard)

Water and gas cooled -100°C to >450°C (special seal)

In-Situ Spectroscopy at High Pressures



High Pressure Reactor

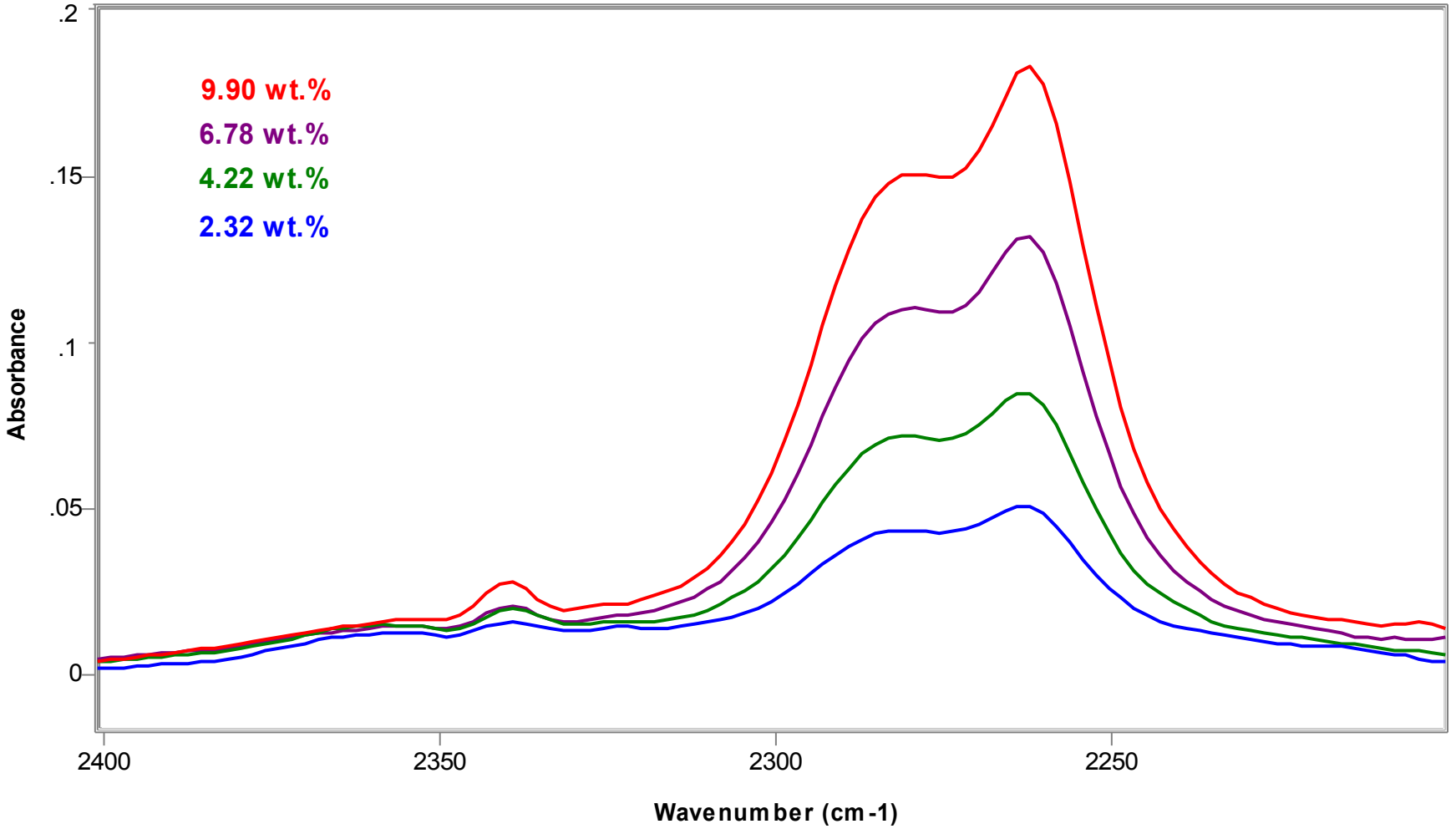
Custom reactor built for use with HP ATR probe

Single hot zone

Water cooling

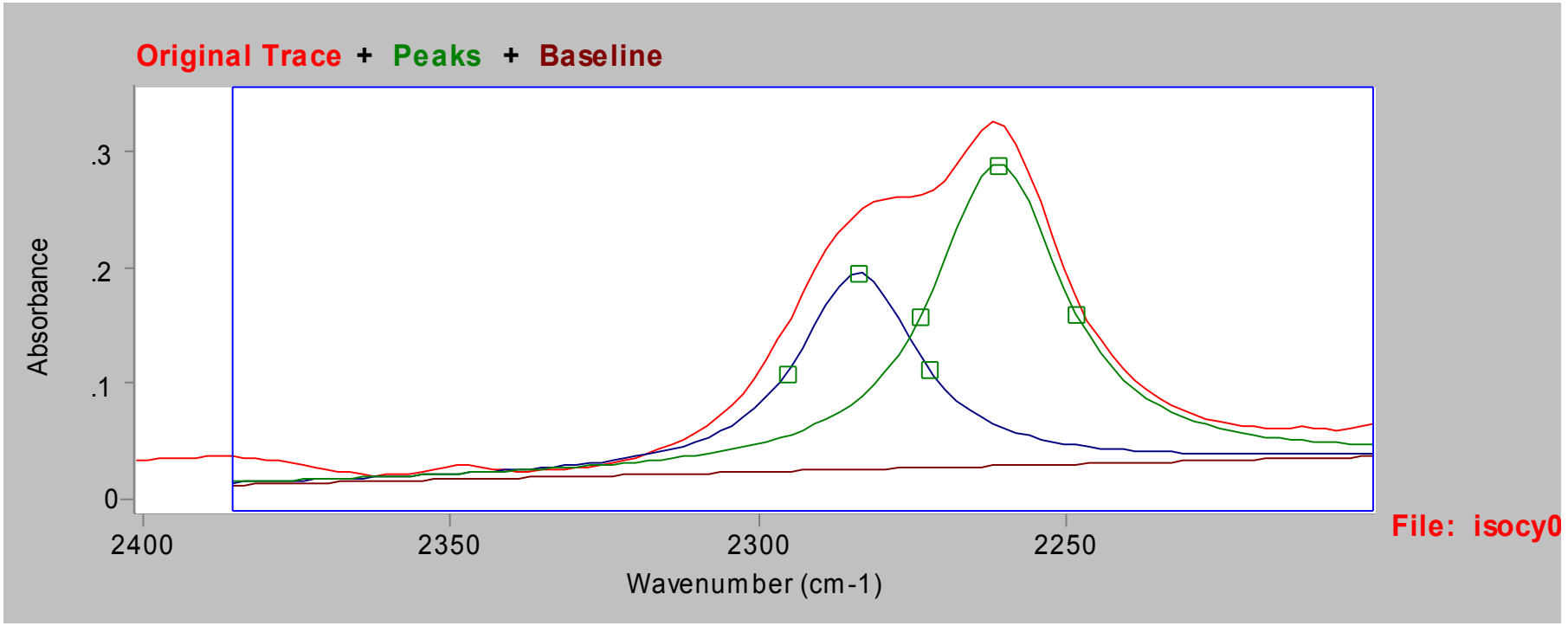
Calibration:

Mid-IR Spectrum of Phenyl Isocyanate in Acetone



Calibration:

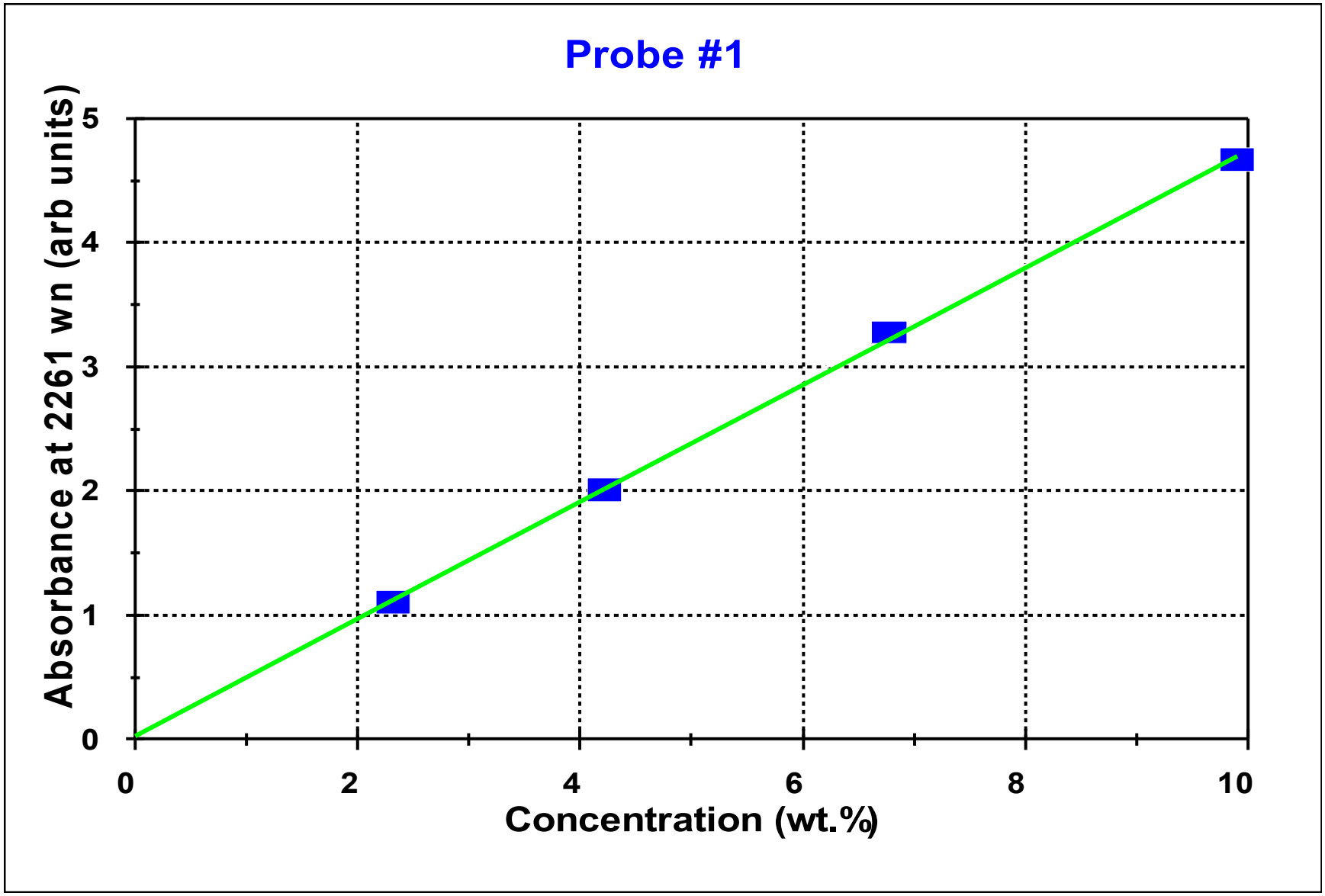
Curve Fitting of 2200-2380 cm^{-1} Region in Mid-IR Spectrum of Phenyl Isocyanate



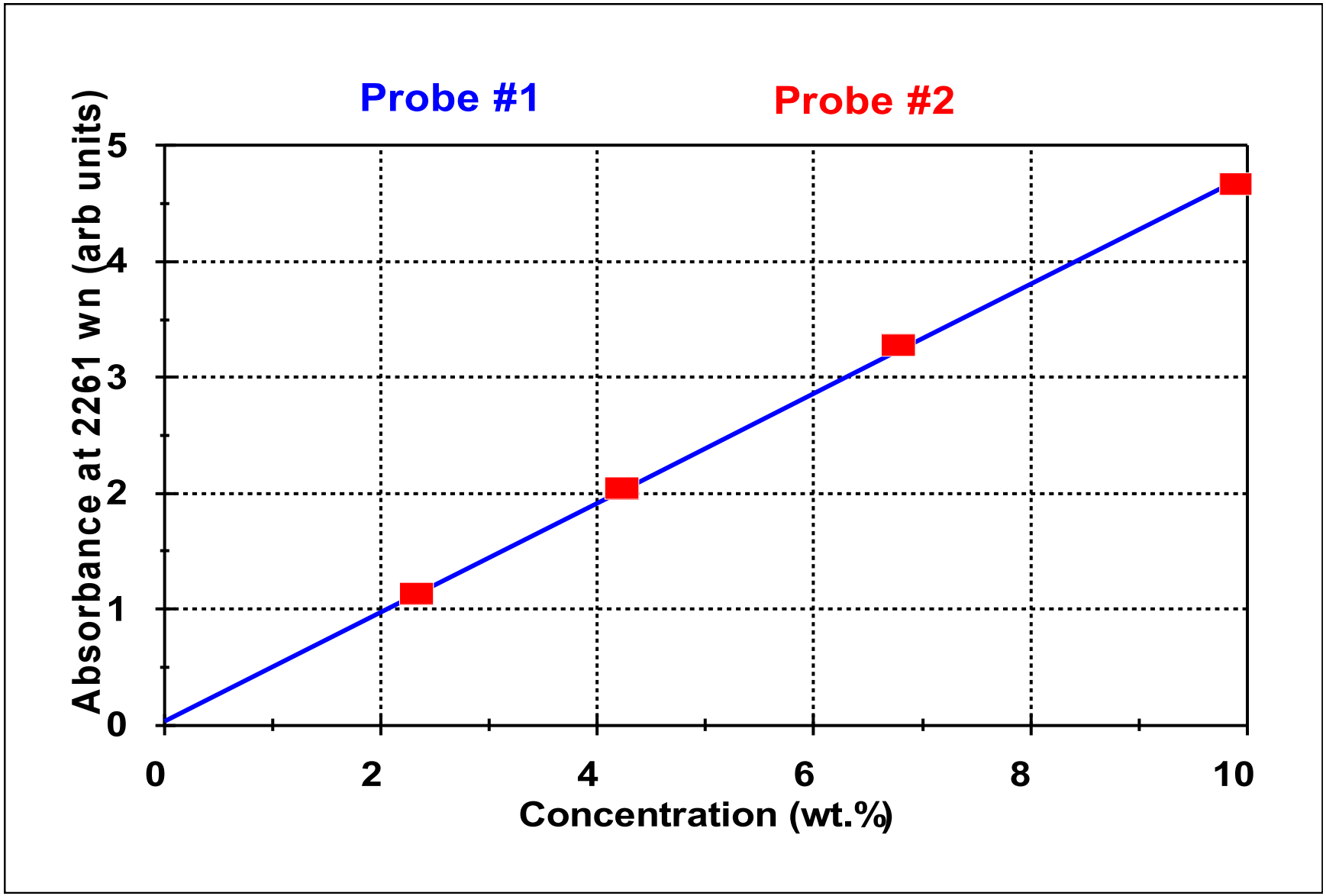
2283 cm^{-1}

2261 cm^{-1}

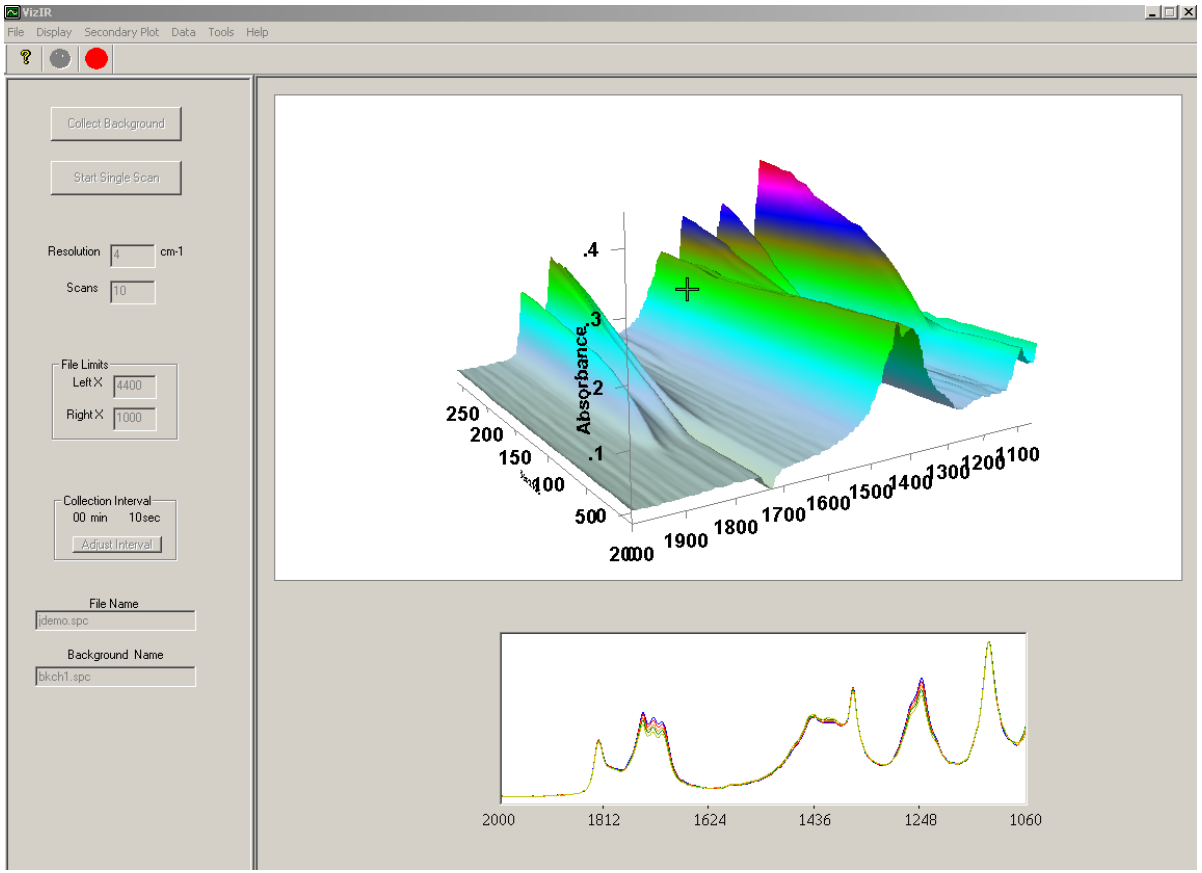
Phenyl Isocyanate in Acetone



Phenyl Isocyanate in Acetone



VizIR™ Software

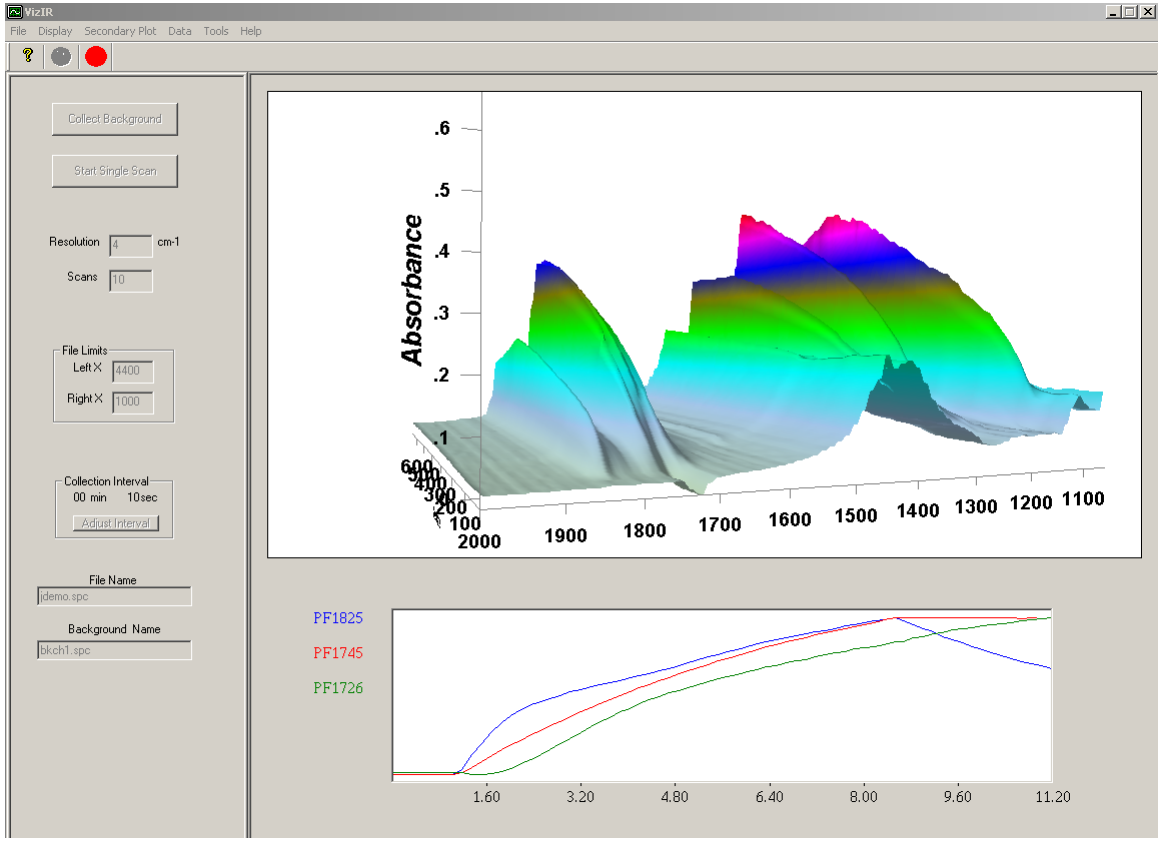


Can collect a single dataset for 3.5 days at one spectrum per minute (5000 spectra)

VizIR includes a Control Panel for setting the resolution and timing of data collection during an experiment, as well as Start and Stop buttons.

The display windows show a 3D picture of the spectra versus time, and a window for most recent spectra or trend-lines.

VizIR Software

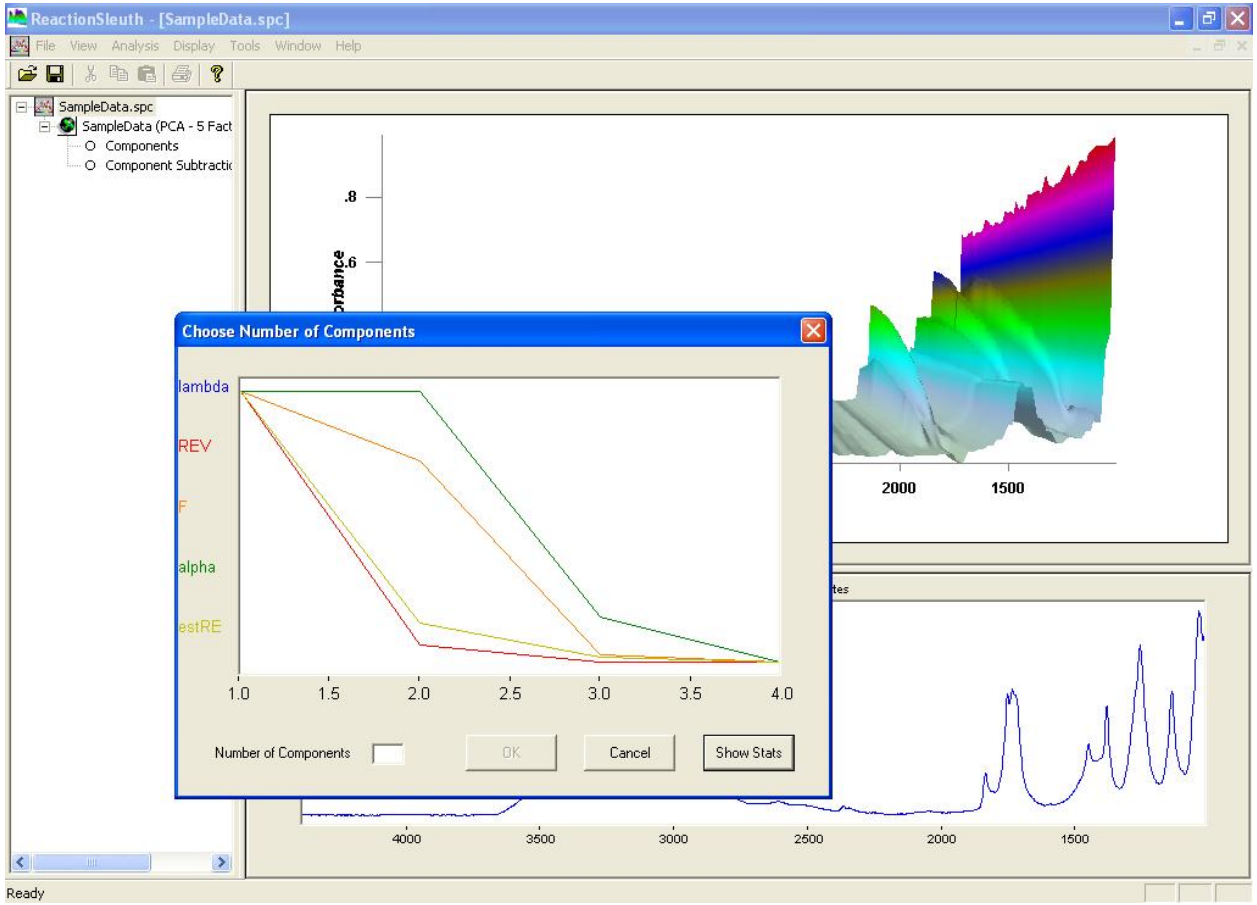


Trend lines can be set up by eye using the Peak-Picker utility, by typing in a desired wavelength, or by using peak fitting (useful for resolving overlapping peaks).

Both products and reactants can be followed.

ReactionSleuth™ Software

REMSPEC



Simple trendlines, baseline corrected lines and ratios of lines.

Peakfit modeling using multiple peak curve deconvolution and fitting of groups of peaks.

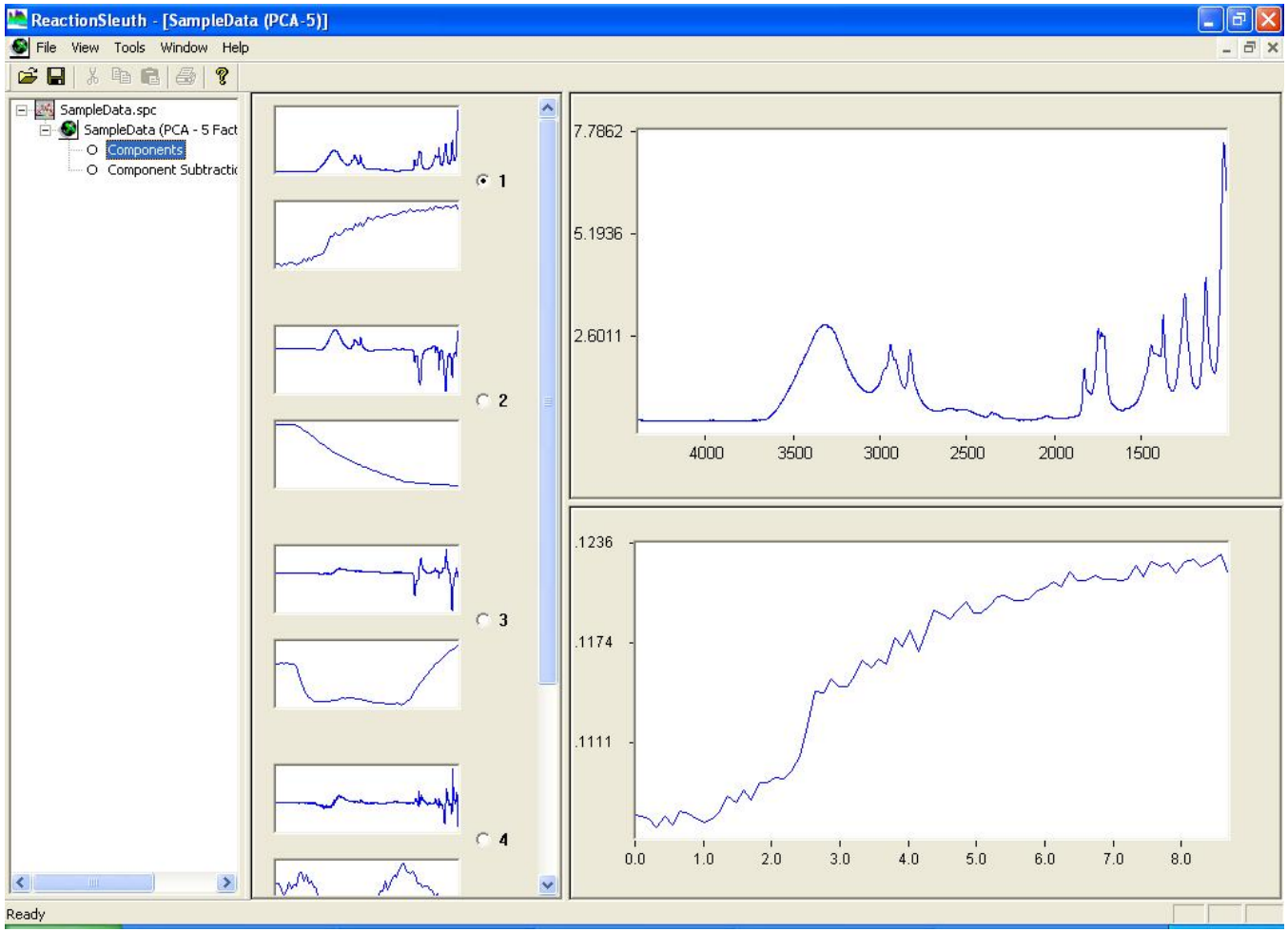
Post processing using PCA/Target Transformation (similar to ConcIRT) for “model free” data analysis

Saved Methods

ReactionSleuth Software

REMSPEC

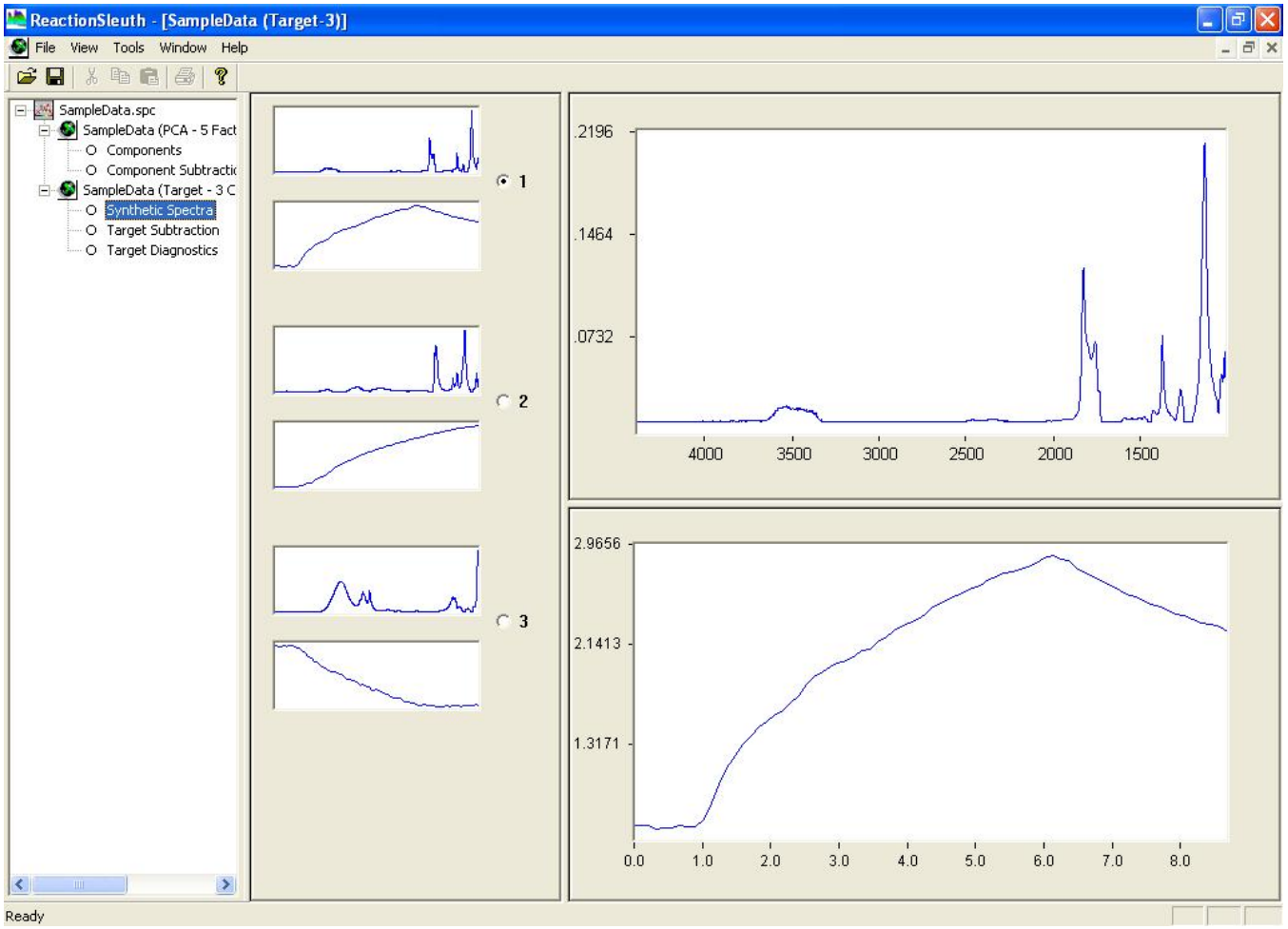
Plots of individual PCA factors and their scores (loadings)



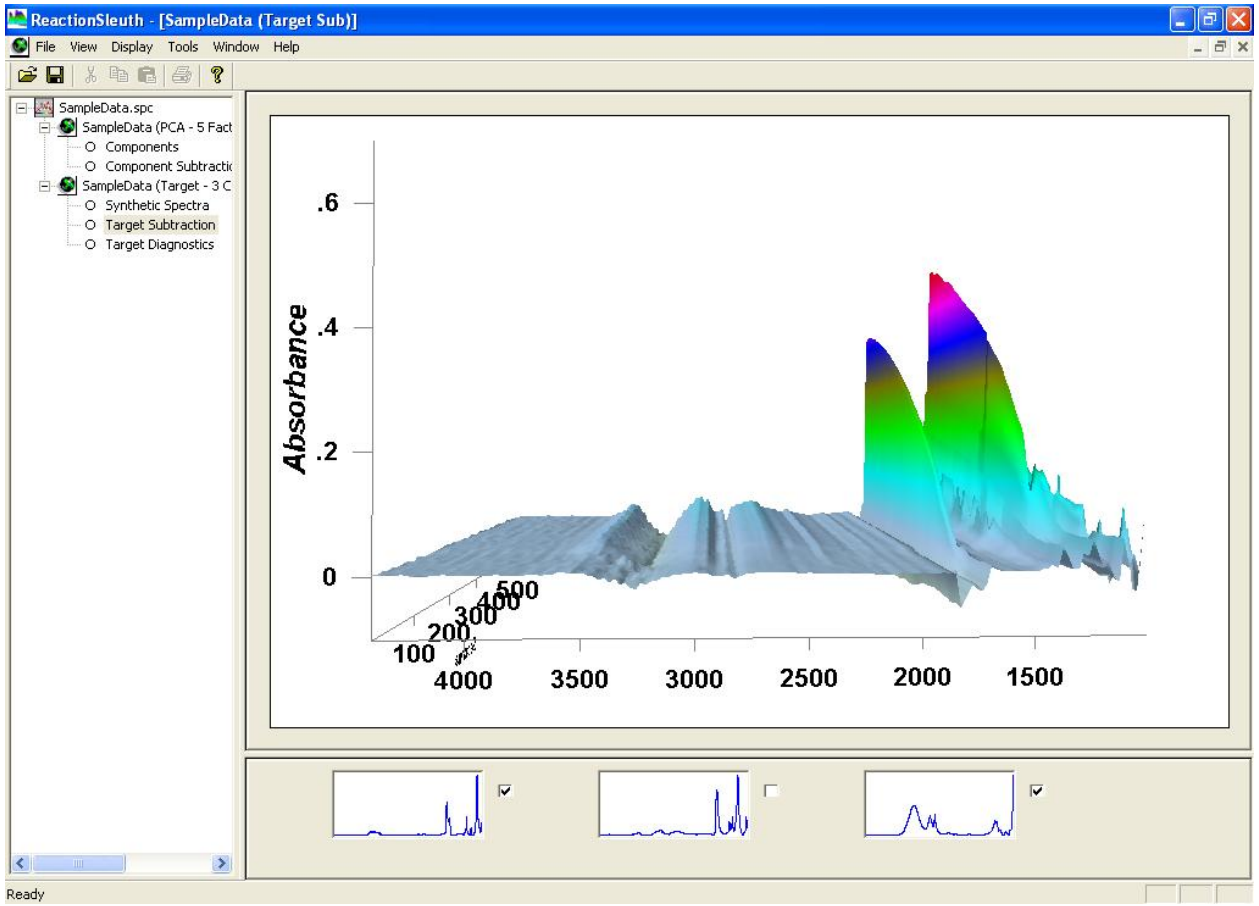
ReactionSleuth Software

REMSPEC

Target transformed “synthetic spectra” and their loadings.



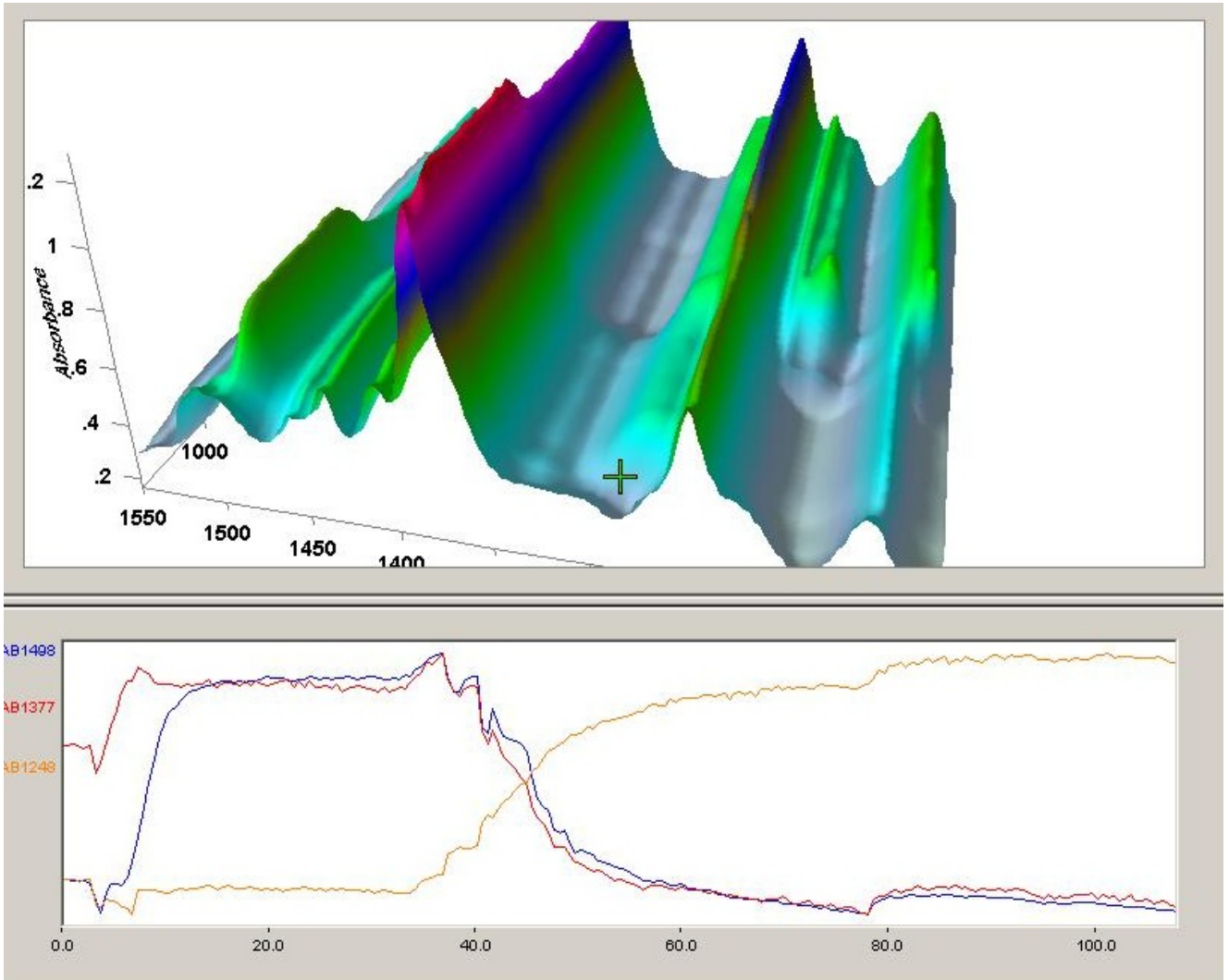
ReactionSleuth Software



Raw data with synthetic spectra subtracted.

This can be useful for identifying side reactions and intermediates.

Example: 2-step Organic Synthesis



2-step commercial synthesis reaction

Step 1

Anion formation

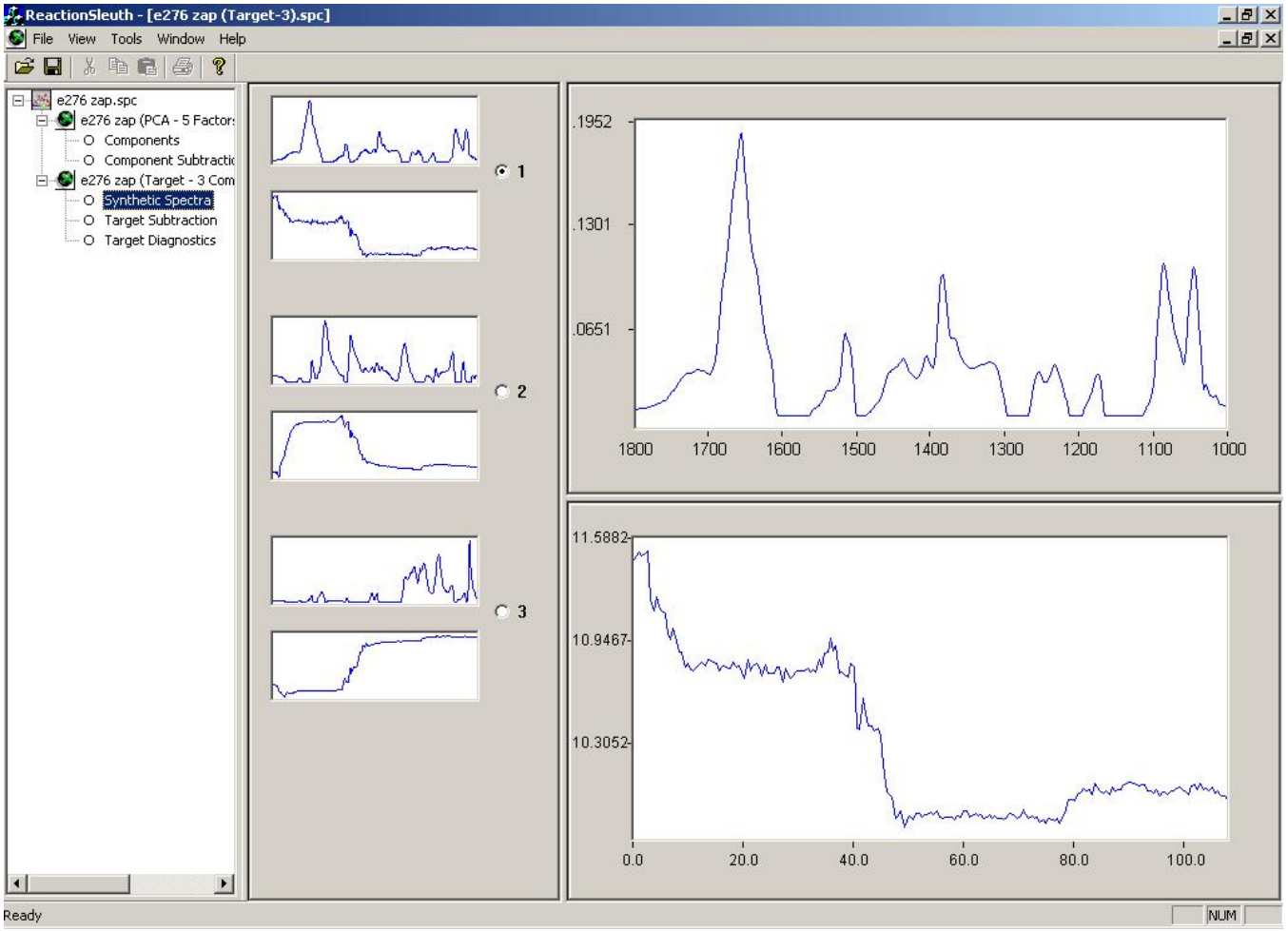
Step 2

Product formation

Solvent is DMF

Note solvent peak at approx. 1400 cm^{-1}.

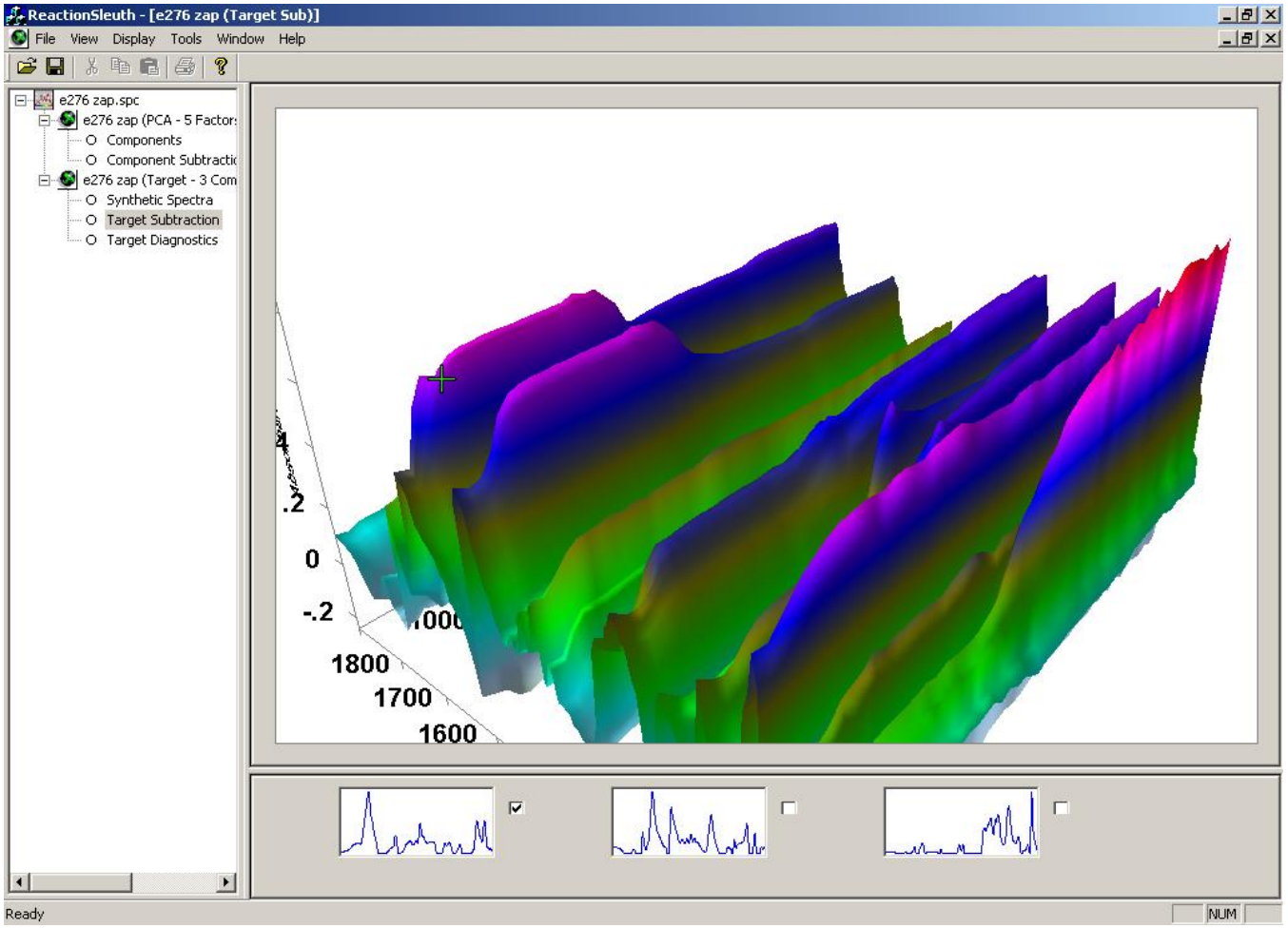
Example: 2-step Organic Synthesis



ReactionSleuth™ can be used to calculate "synthetic spectra" using a PCA/Target Transform technique.

A set of three synthetic spectra is shown here, with the "loading" curve for each, showing the changes in the contribution of each synthetic spectrum to the data set over time.

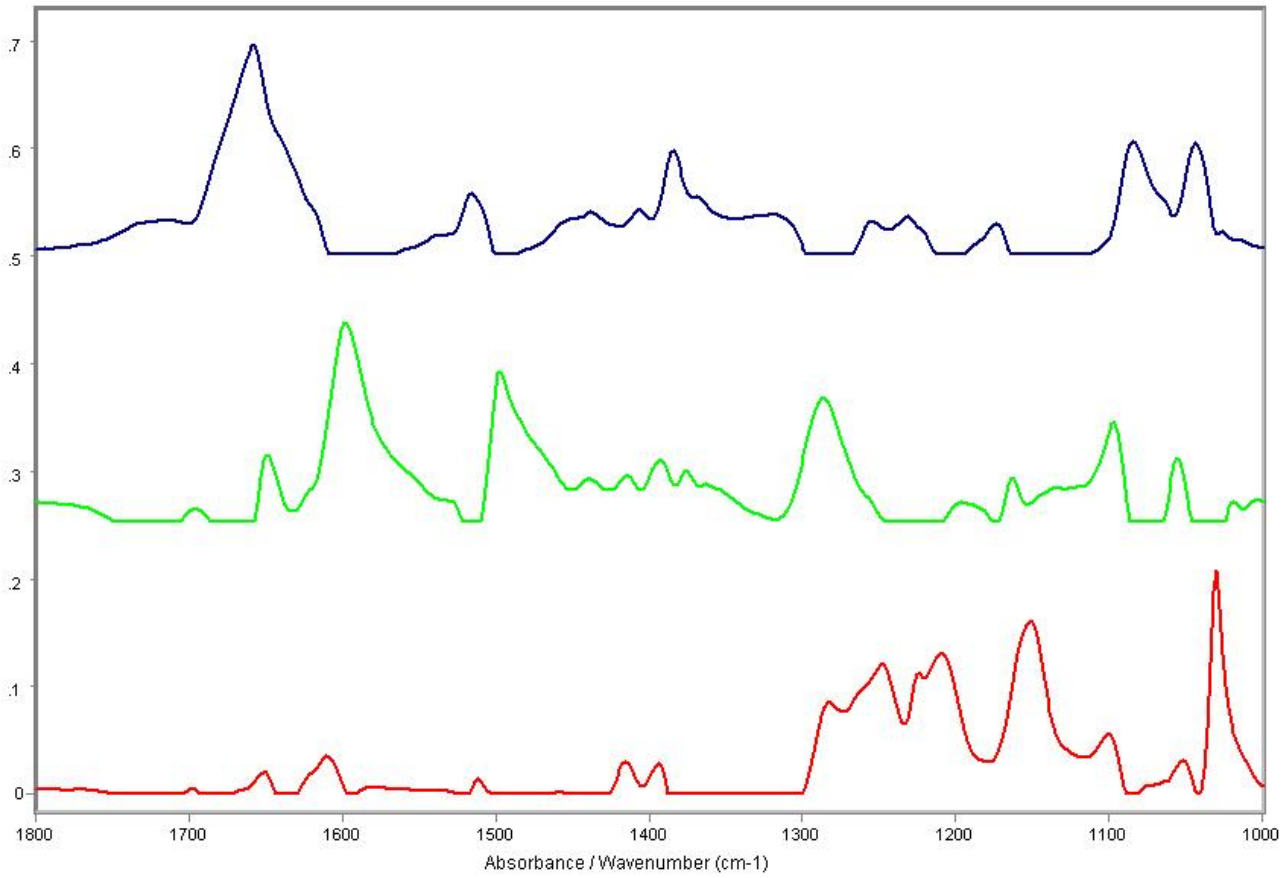
Example: 2-step Organic Synthesis



The 3D display shown here is the result after one of the three synthetic spectra has been subtracted from the data set.

The subtracted spectrum (shown in blue on the next slide) closely resembles the mid-IR spectrum of the DMF solvent.

Example: 2-step Organic Synthesis



The upper, blue, trace is a synthetic spectrum that closely resembles that of DMF.

The second, green, trace is a synthetic spectrum that appears and disappears during the reaction, so we have extracted the spectrum of an intermediate and its time/concentration behaviour.

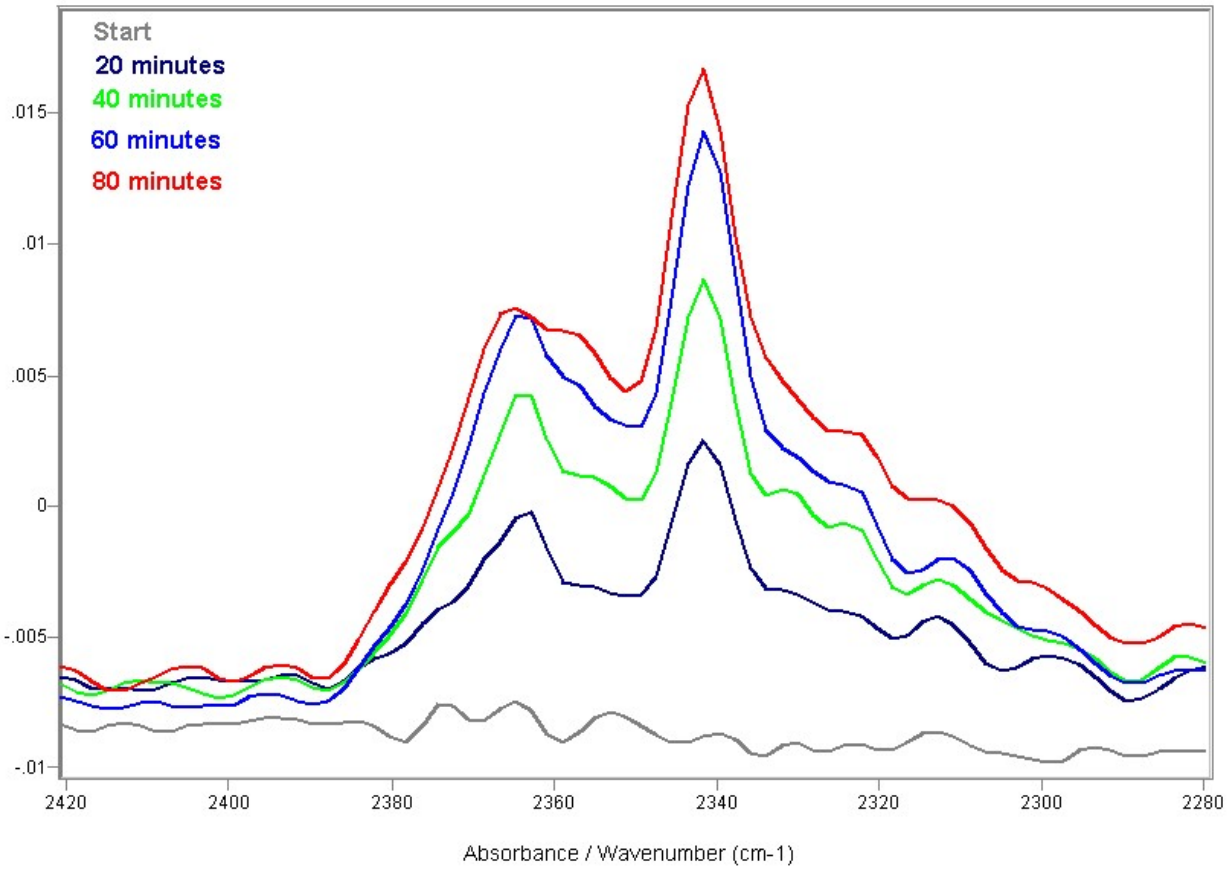
The third, red, synthetic spectrum, can be identified as the product.

Fermentation Monitoring

- Cloudy, aqueous medium with varying optical density
  - ATR in the mid-IR samples only the liquid phase and is not affected by suspended solids or varying optical density

Fermentation Monitoring

Carbon dioxide region

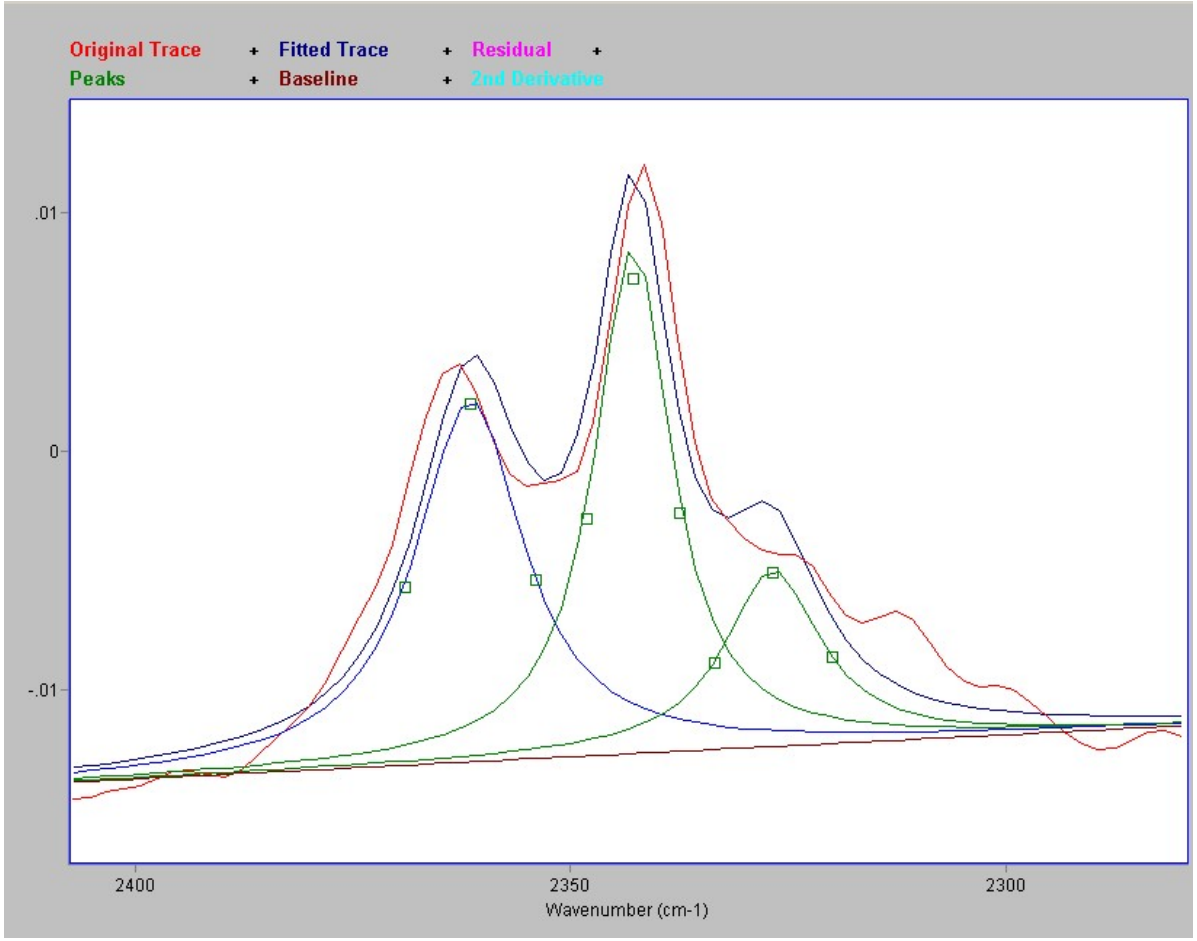


A single peak emerging at 2342 cm^{-1} is characteristic of dissolved CO_2, and a robust calibration has been developed.

The neighboring peaks are associated with other forms of CO_2, e.g. contained in small bubbles; these features are hard to calibrate.

Fermentation Monitoring

Carbon dioxide region



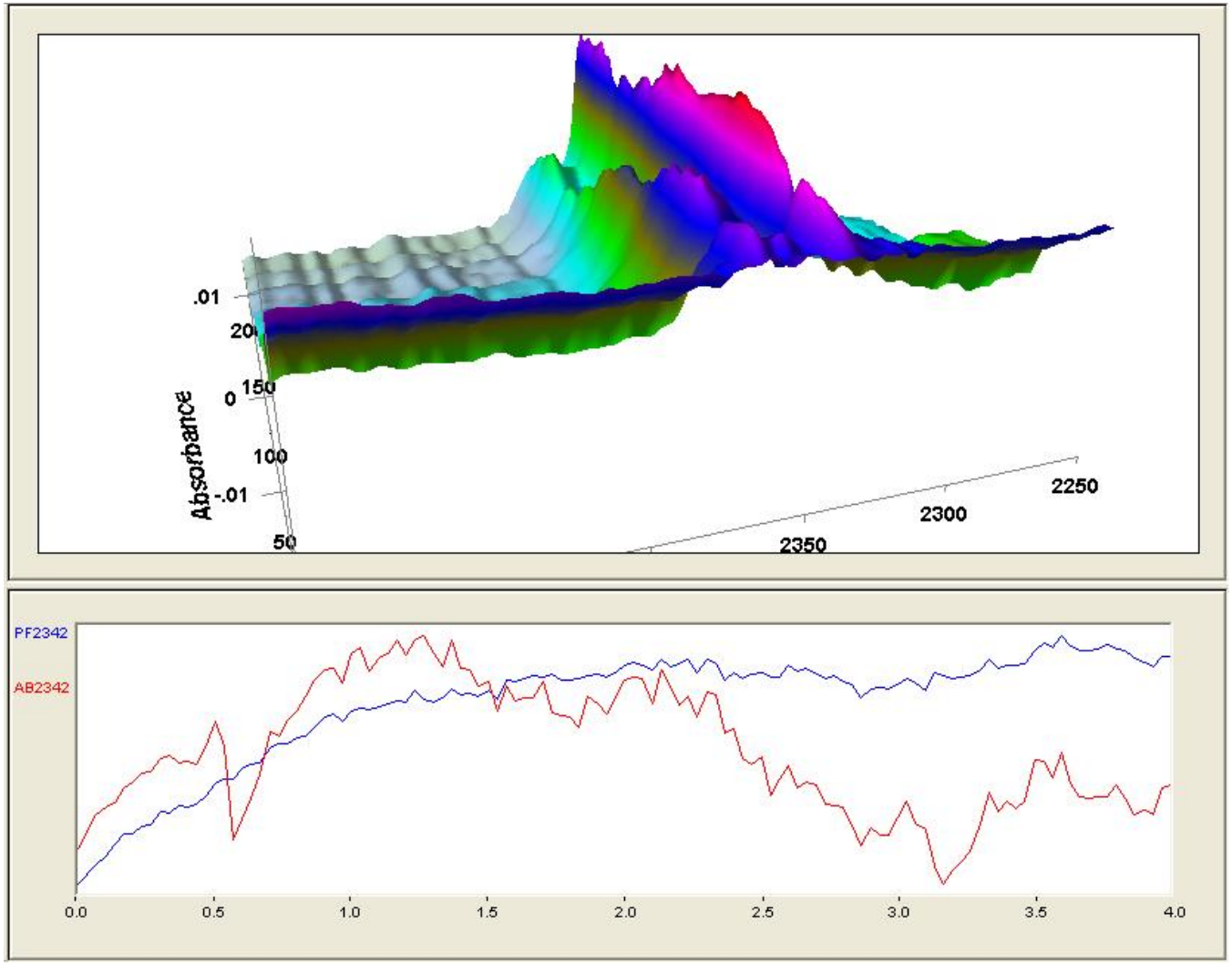
The calibration is based on a peak-fitting model of the CO_2 spectral region.

VizIR can run the model in real time as spectra are collected, to generate a trendline.

The peak at 2342 cm^{-1} can be calibrated against known dissolved CO_2 concentrations.

Fermentation Monitoring

Carbon dioxide region



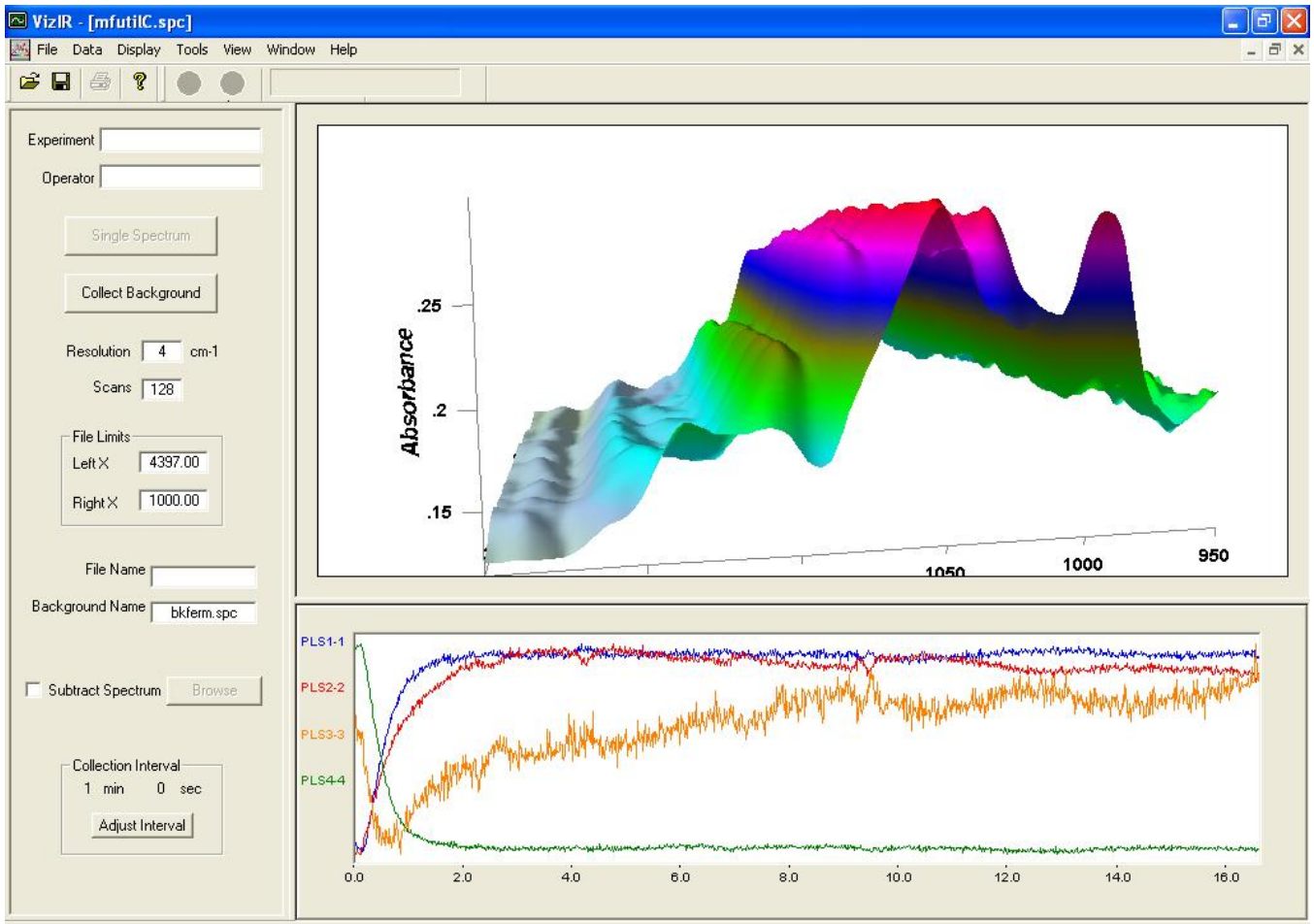
The changes in the CO_2 region are clearly visible in the 3D display.

The blue CO_2 trendline is based on the peak at 2342 cm^{-1} from the peak-fit model

Compare with the simple line based on the intensity at 2342cm^{-1}.

Fermentation Monitoring

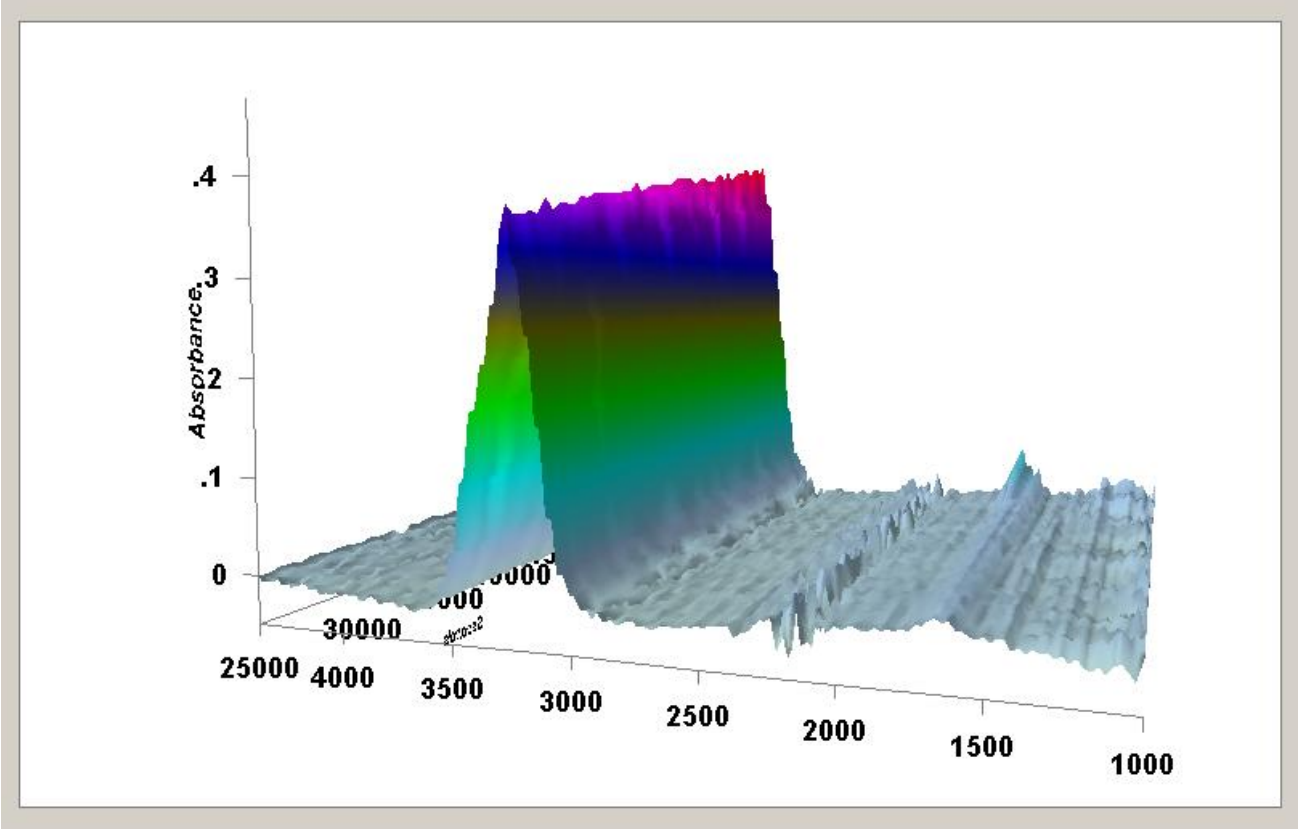
Calibration of Trendlines



PLS models based on a set of solutions of sucrose, fructose, and glucose, and ethanol can be run in real time.

Note that these trendlines are individually autoscaled.

ReactionView Spectra of Oxidative Oil Degradation

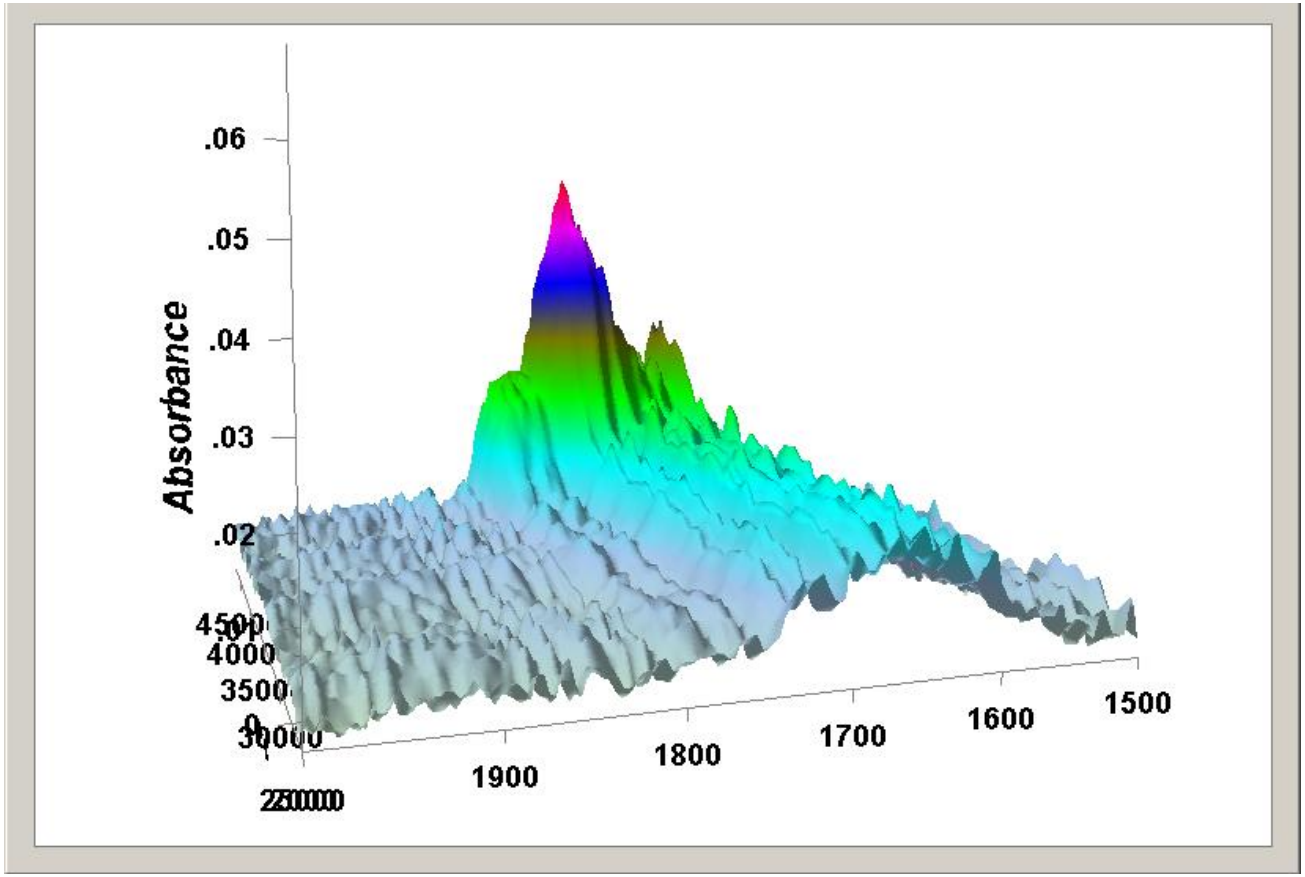


ReactionView dataset from 1000-4500 cm^{-1} (a baseline correction has been applied to each spectrum).

Shows changes between reaction time 420 min. and 800 min.

Note emergence of feature centered at approx. 1700 cm^{-1}, the carbonyl region.

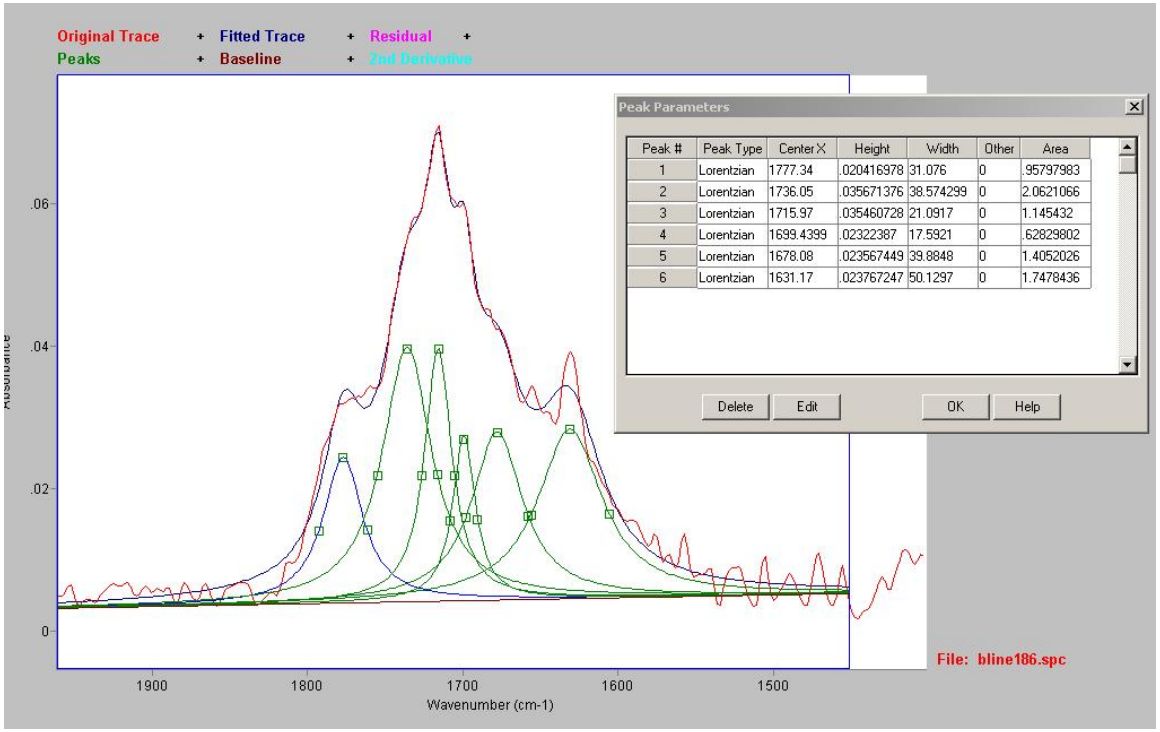
ReactionView Spectra of Oxidative Oil Degradation



The emerging carbonyl feature is quite complex.

The VizIR software that runs ReactionView can be used to set up trendlines based on peak-fitting models.

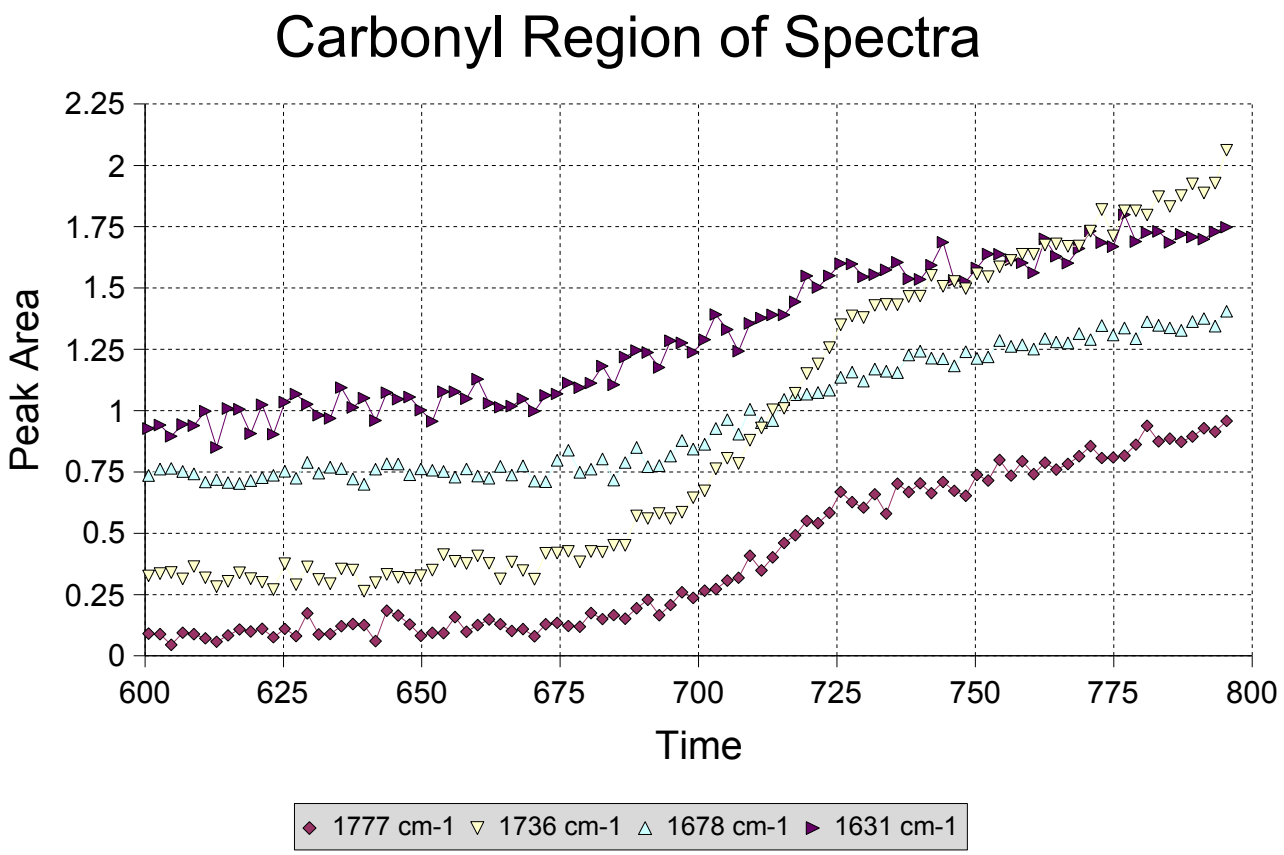
Peak-Fit Model of ReactionView Data



Model is based on the final spectrum in the set.

VizIR calculates trendlines by fitting the model against each spectrum in the set, either in realtime or in post-processing.

Trendlines from Oil Degradation Spectra

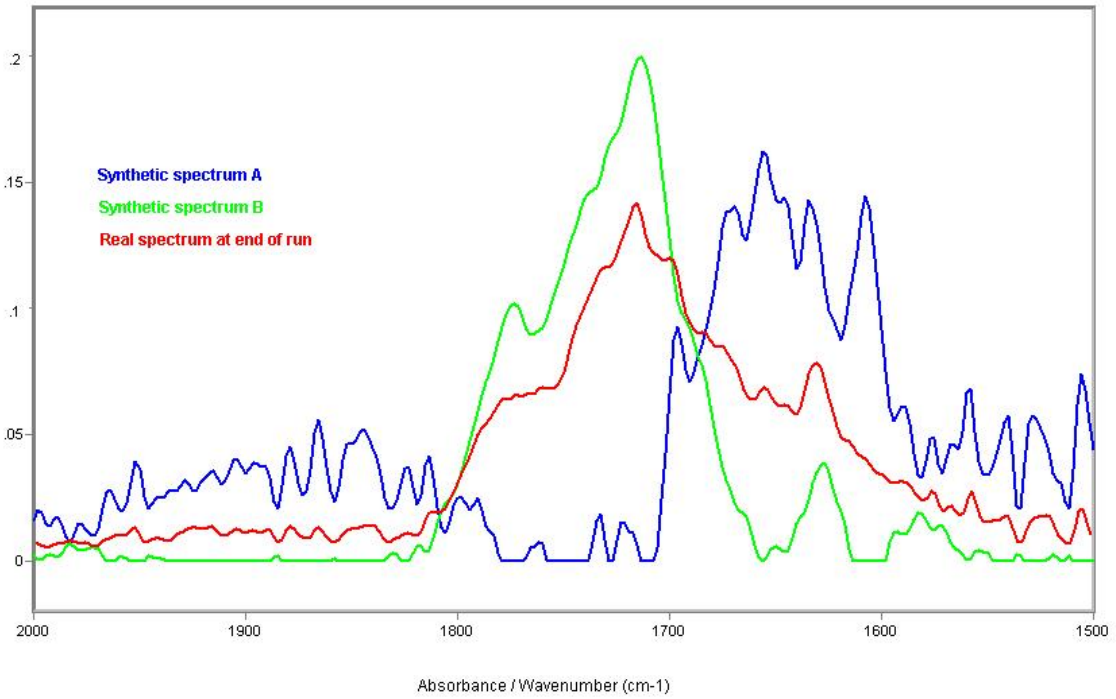


The peak areas from the model of the carbonyl region are graphed against time (in minutes).

It is possible to distinguish different times of onset, and different rates of emergence for different peaks.

The peaks at 1777 and 1736 cm^{-1} grows more rapidly that the others.

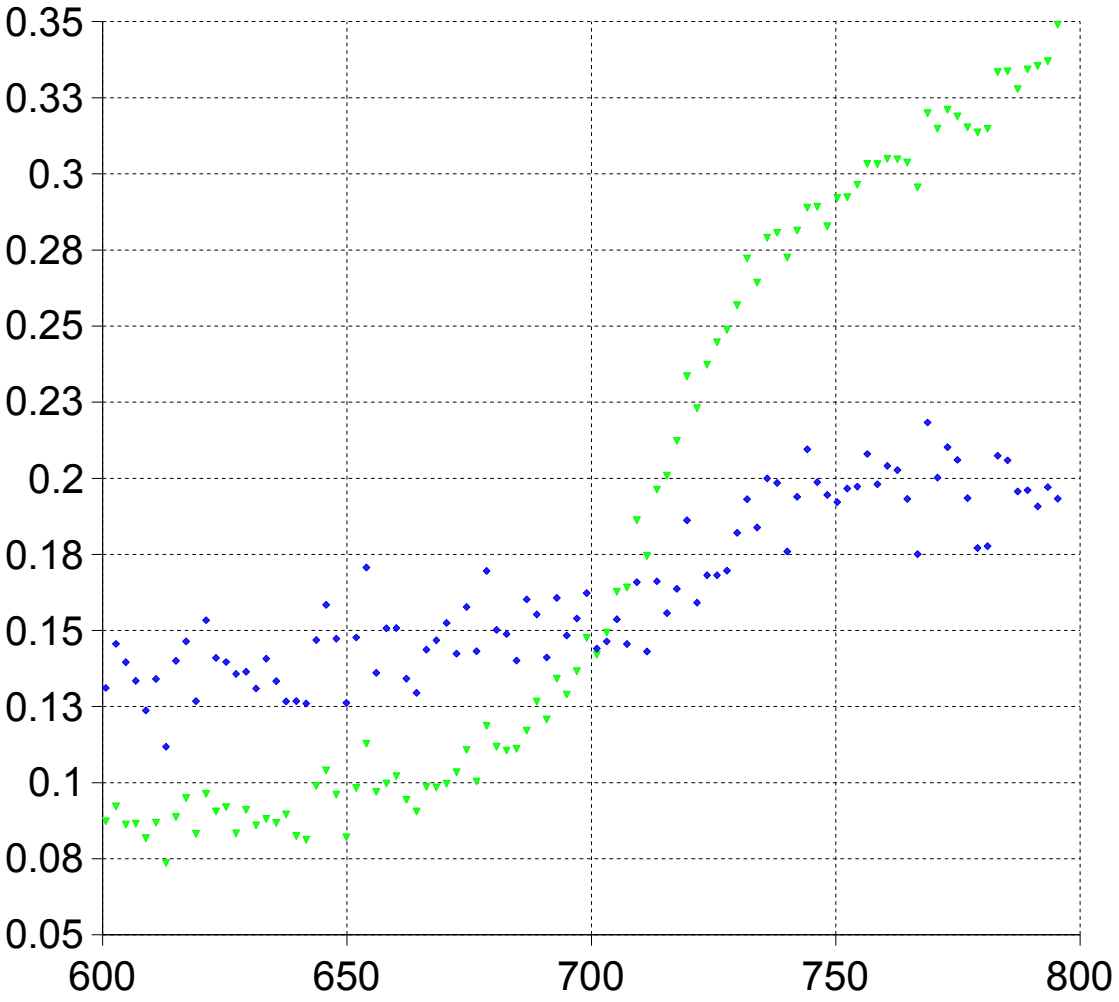
Synthetic Spectra Calculated from Oil Degradation Data



When Remspec's ReactionSleuth software is used to calculate "synthetic spectra" from the dataset, the two spectra shown in blue and green are obtained.

The red trace is the spectrum from the end of the ReactionView run.

Trendlines Calculated for Synthetic Spectra



The two synthetic spectra show different trending behavior.

This confirms the conclusion from the peak-fit trends that two distinct processes are taking place at different rates, and at different induction times.

Process 1: starts around 680 minutes, relatively fast.

Process 2: starts around 700 minutes, relatively slow.

In Summary

Remspec manufactures and supplies mature, well supported systems with a wide choice of sampling options that are easy to use and provide repeatable data.

Remspec provides specialized software that is optimized specifically for reaction monitoring and the analysis of reaction data.