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mIRage+R sample report

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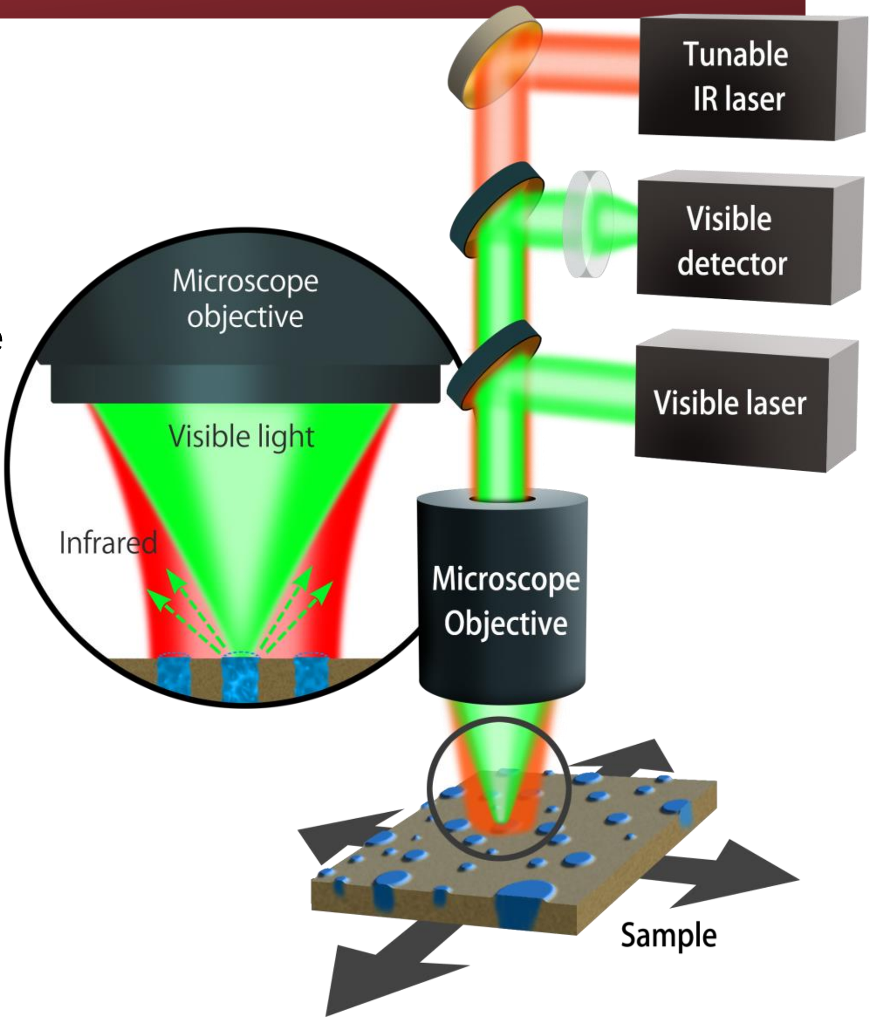
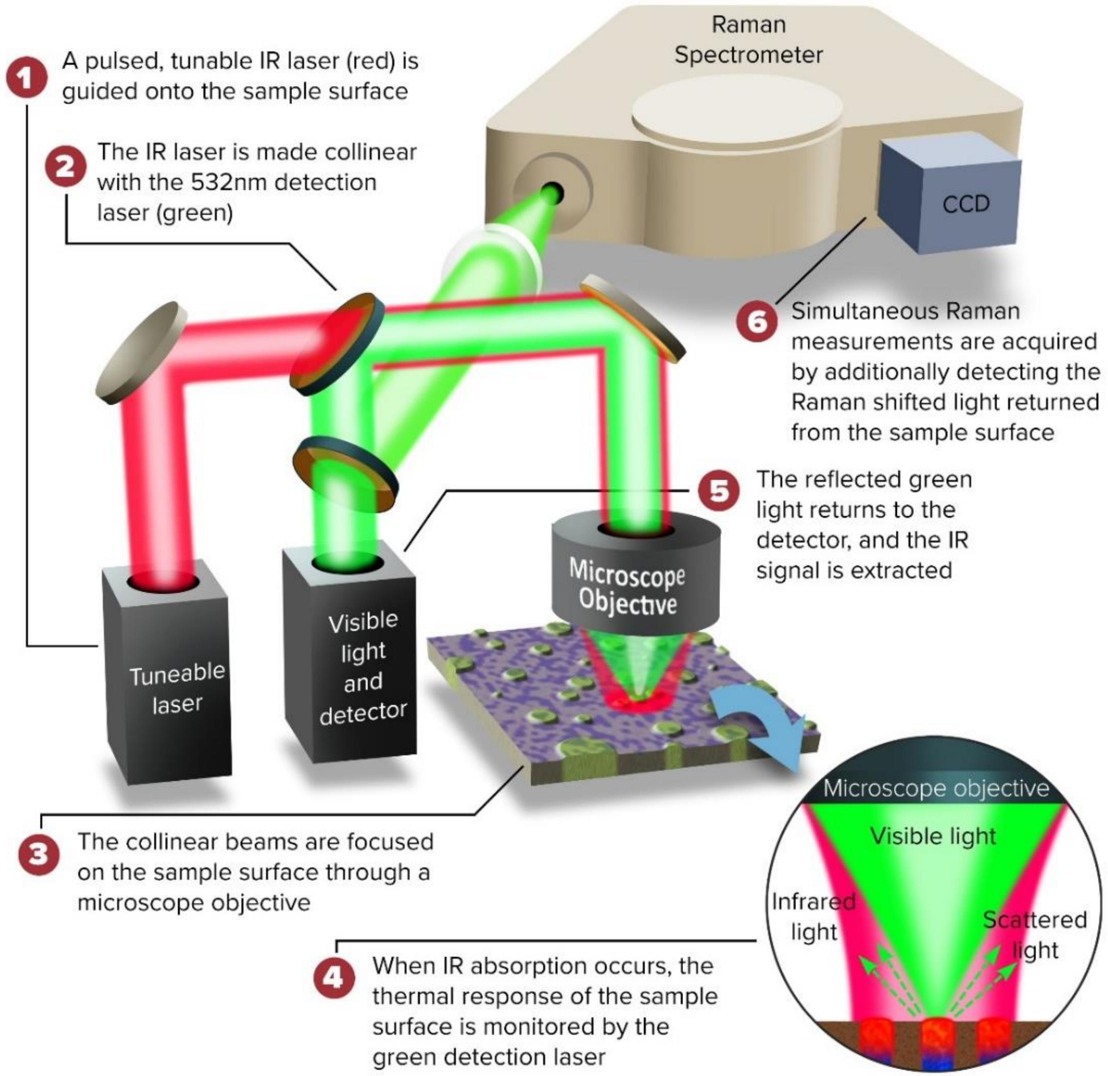
mIRage™: Optical PhotoThermal IR Spectroscopy

- Photothermal physics to measure IR absorption spectra:
  - IR laser beam focused on sample
  - Absorbed IR light causes sample to heat up, creating a photothermal response in the sample
  - Visible probe measures the photothermal response due to IR absorption
- Use of visible light allows submicron resolution, independent of IR wavelength
- Optical microscope based technique
- FTIR transmission quality spectra in reflection mode
- Easy to operate
- Fast spectra ~ 1 sec



IR+Raman


Raman
Spectrometer
CCD
1 A pulsed, tunable IR laser (red) is guided onto the sample surface
2 The IR laser is made collinear with the 532nm detection laser (green)
6 Simultaneous Raman measurements are acquired by additionally detecting the Raman shifted light returned from the sample surface
5 The reflected green light returns to the detector, and the IR signal is extracted
Microscope Objective
Tuneable laser
Visible light and detector
3 The collinear beams are focused on the sample surface through a microscope objective
4 When IR absorption occurs, the thermal response of the sample surface is monitored by the green detection laser
Microscope objective
Visible light
Infrared light
Scattered light

Summary

- Three samples were examined
  - 1. Sample K-03
  - 2. Sample C-8
  - 3. Sample D-1

- Individual paint chips were placed in a micro-vice and cross sectioned using a microtome. The bulk sample was examined, no collection of sections is necessary.

- Each sample was examined with multiple IR sources, a QCL laser covering 800 – 1800 cm^{-1} and an OPO laser covering 2700 – 3600 cm^{-1}. Additionally, both 532 and 785 nm visible lasers were used for collection of both mIRage and Raman spectra.

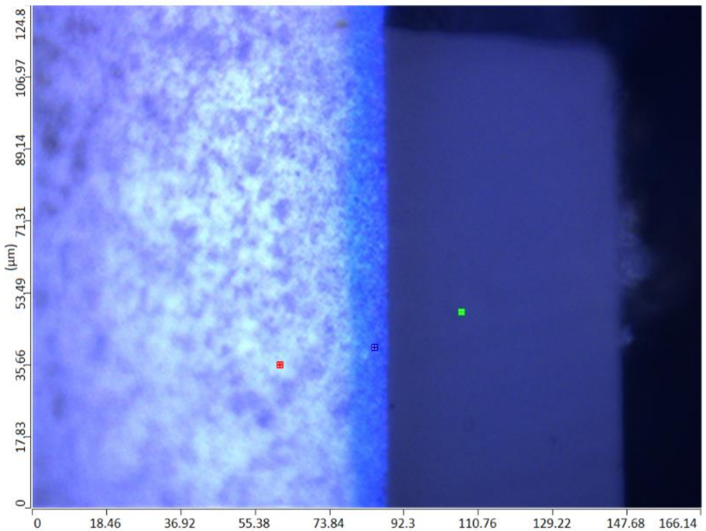
- mIRage point spectra, line arrays and hyperspectral datasets were collected along with simultaneous Raman spectra from several locations on each sample.

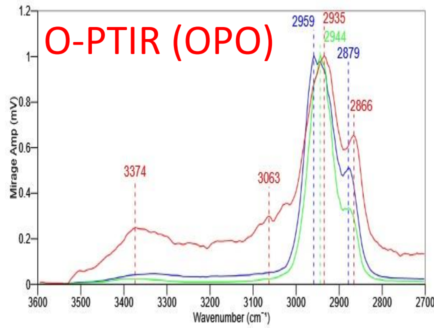
- KnowItAll database searching identifies various materials layers, as well as pigments.

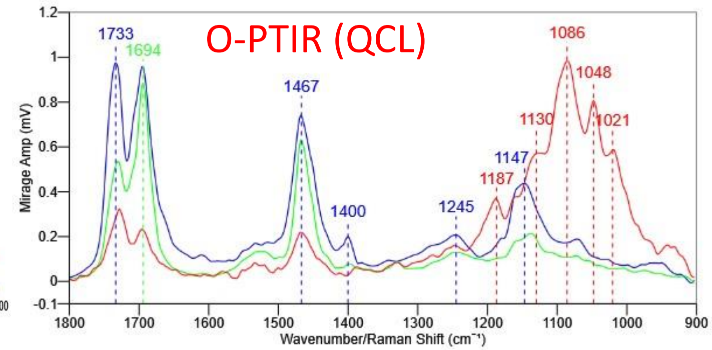
- mIRage single frequency imaging and hyper spectral imaging highlights the distribution of various chemical species throughout the various layers within the samples.

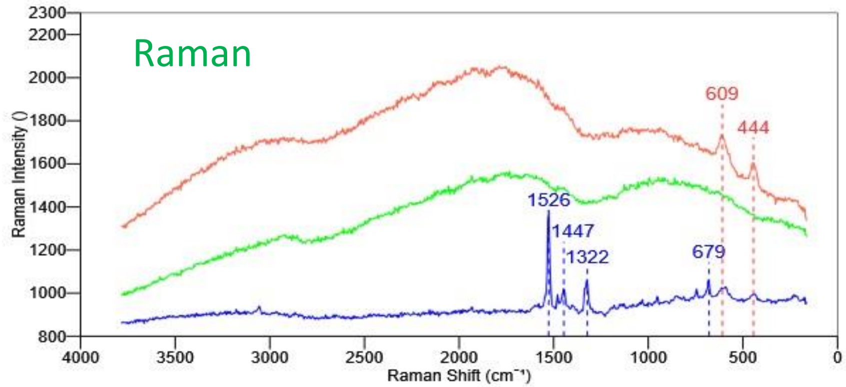
Optical image of Sample K (right side)

mIRage 40x optical image



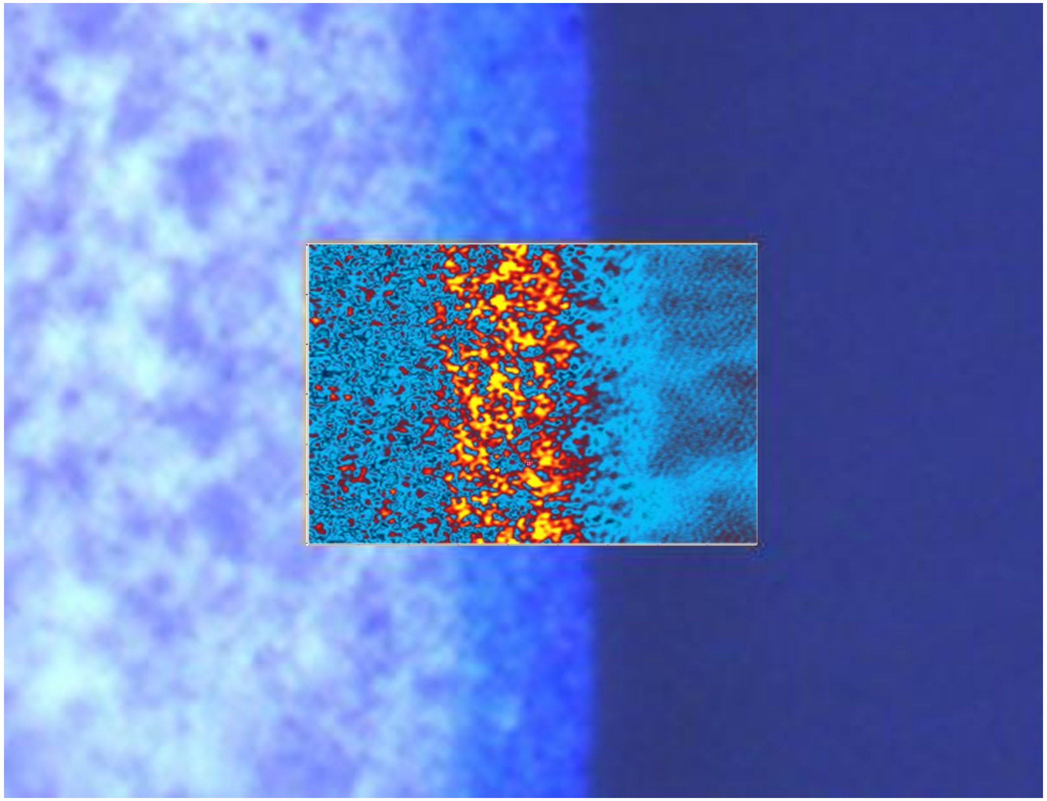






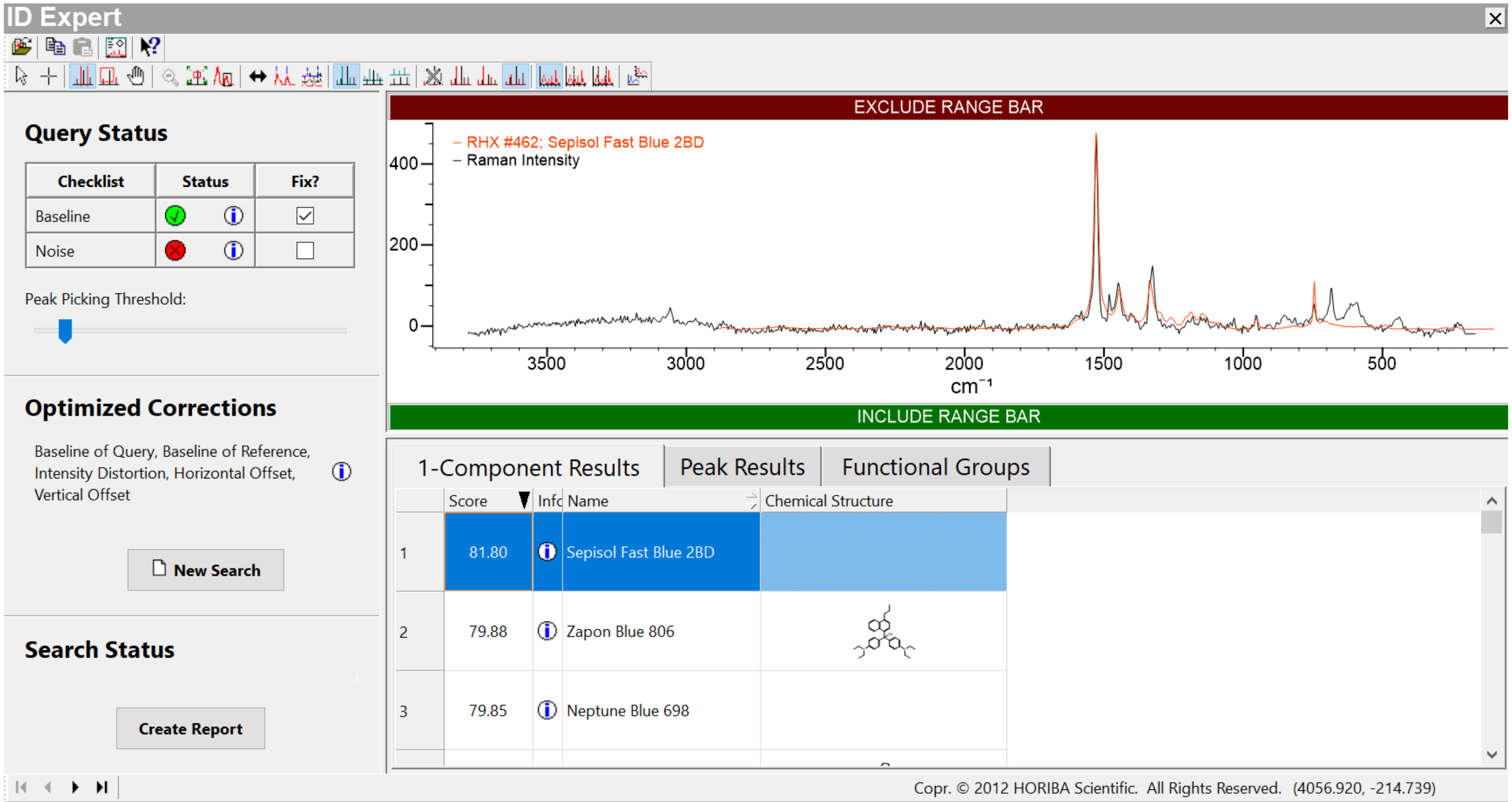
- Markers on image indicate the location of subsequent mIRage spectra
- mIRage QCL spectra show significant differences between layers, with the carbonyl ratio varying significantly between pigment layer (blue) and surrounding layers. Additionally, significant C-O stretching vibrations are observed in the interior layer(red)
- mIRage OPO spectra also show significant differences between layers, with differences observed in the C-H stretching region (2800 – 3100 cm^{-1}). Additionally, significant O-H stretching vibrations (3374 cm^{-1}) are observed in the interior layer(red)
- Raman spectra collected from each layer show clear spectral differences. Very low laser power (< 1 mW) was used during data collection to minimize fluorescence contributions. Fluorescence was still present in certain layers (red and green), obscuring Raman peaks. Clean spectra were collected from thinnest layer and are identified on the following slide using the KnowItAll database.

mIRage single frequency imaging



- mIRage QCL single frequency image captured at 1733 cm^{-1} highlights the interior pigment layer. This layer shows significant domain formation within, most likely a result of the inorganic pigment that is dispersed throughout.

KnowItAll Raman database searching



- KnowItAll Raman database searching identifies the thinnest layer within the sample as a blue dye material. The database used for spectral identification was the Horiba-Forensics Raman database.

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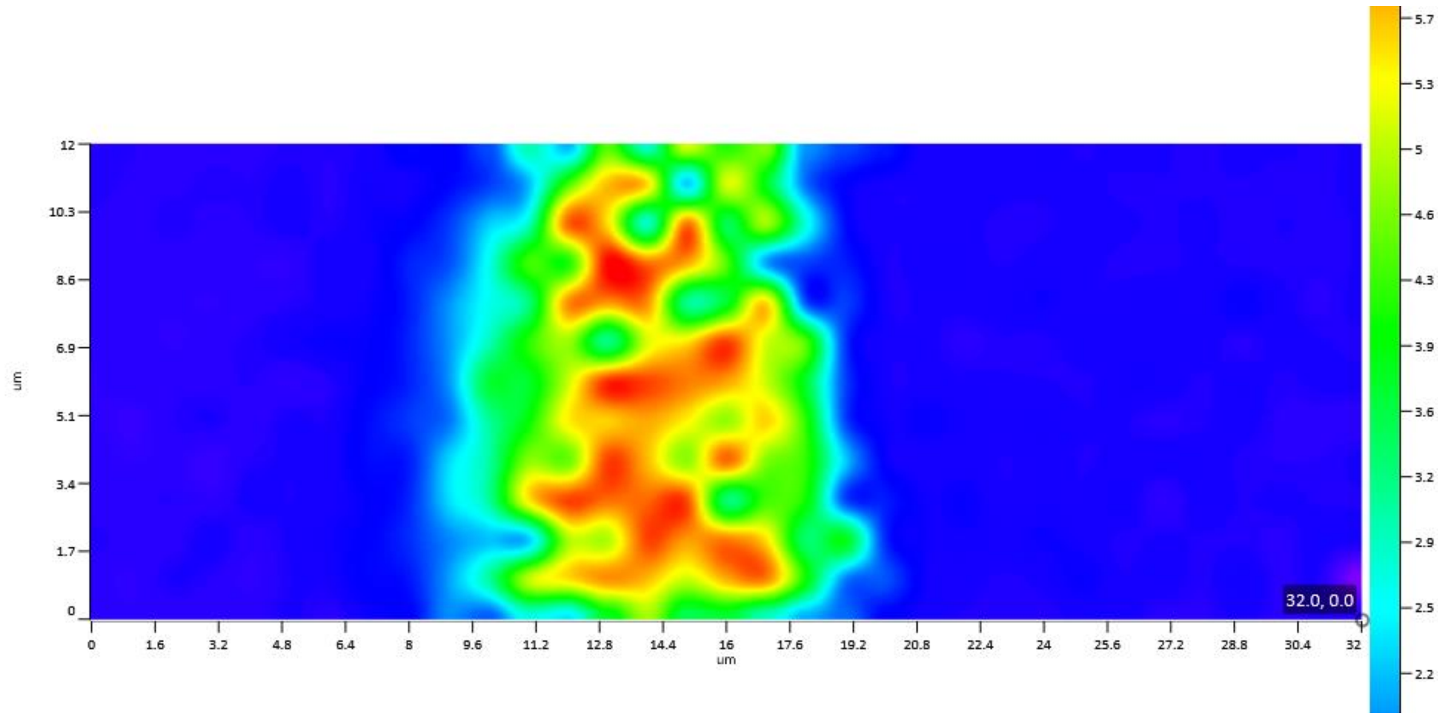
Raman hyperspectral imaging of right side layers



- This Raman hyperspectral image displayed at 1520 cm^{-1} highlights the distribution of the pigment identified on the previous slide. Each pixel in this image has a complete Raman spectrum. Data was collected with a 785 nm laser and at 1 µm spacing in X and Y.

785 nm visible laser was used.

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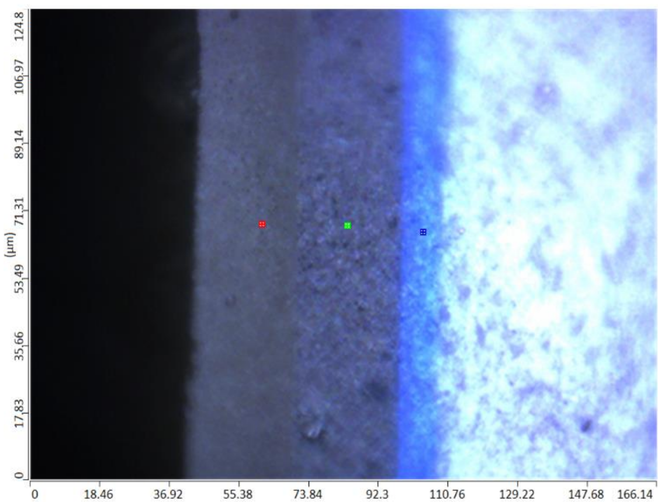
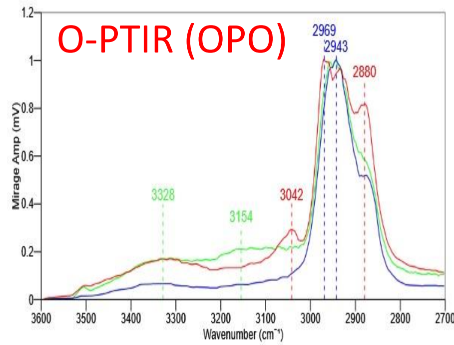
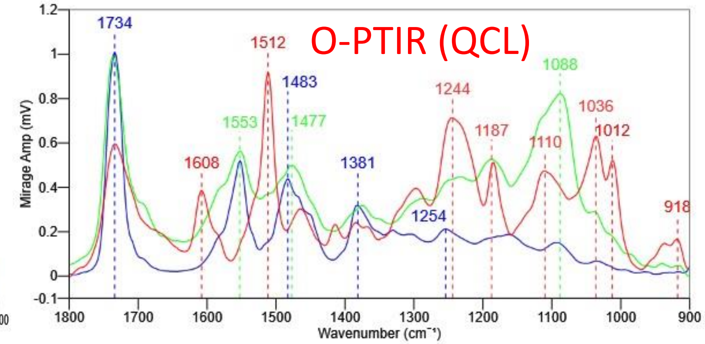
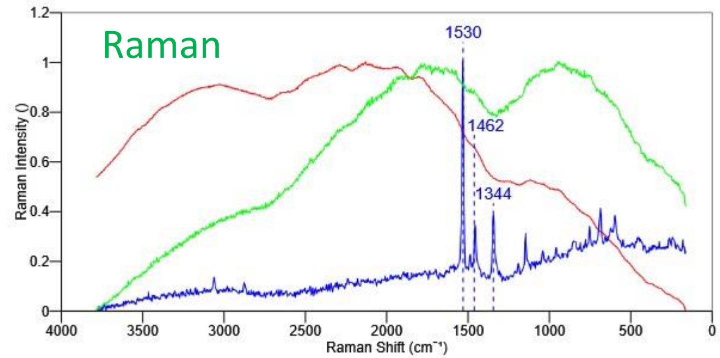
Optical image of Sample K (left side)

mIRage 40x optical image



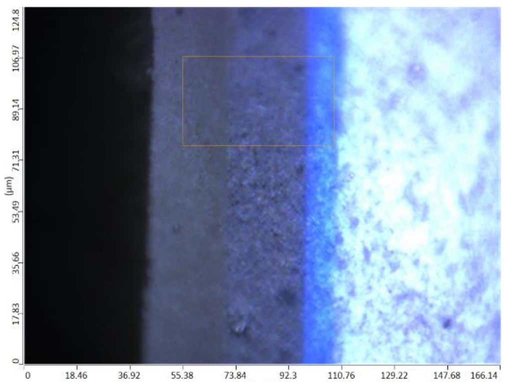




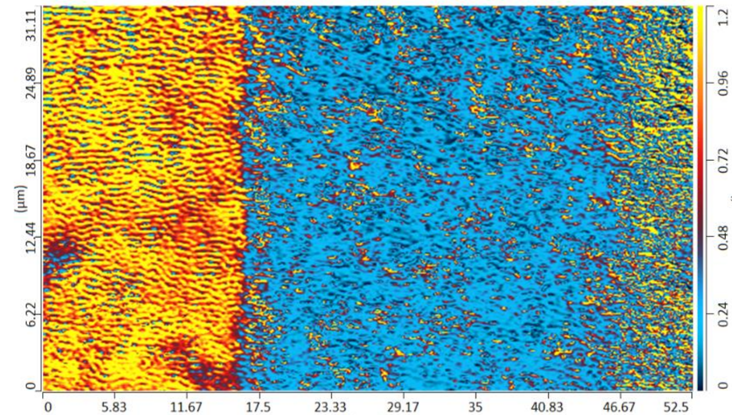


- Markers on image indicate the location of subsequent mIRage spectra
- Once again Raman spectra were collected at low power < 1 mW to minimize the effects of fluorescence.

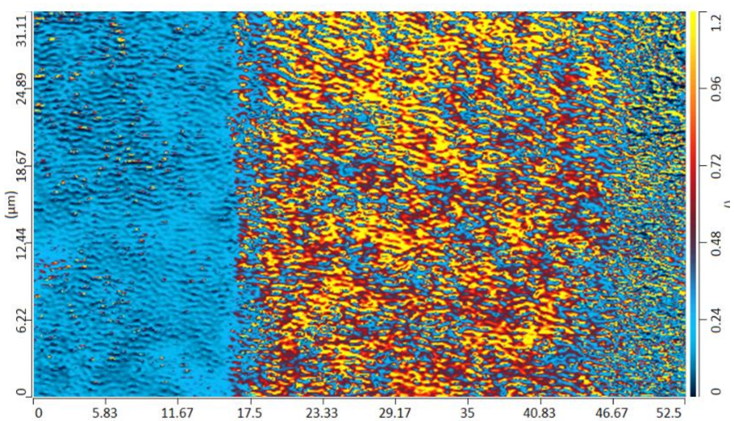
mIRage single frequency imaging



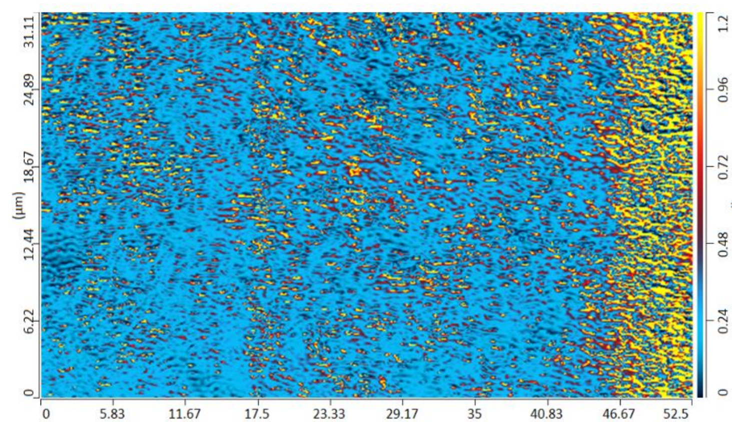
mIRage 40 x optical image
(orange box represents border for mIRage images)



mIRage image ratio 1512/1736 cm^{-1}



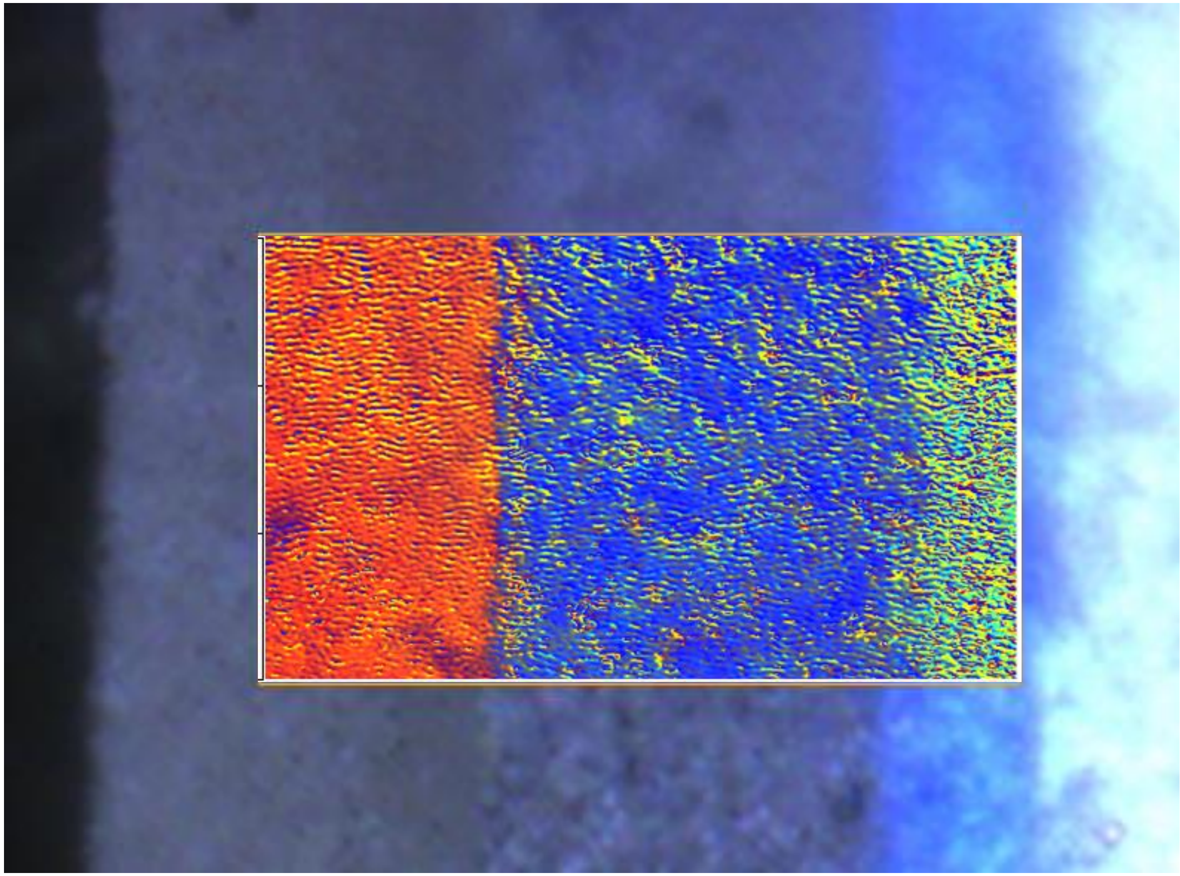
mIRage image ratio 1736/1512 cm^{-1}



mIRage image ratio 1088/1736 cm^{-1}

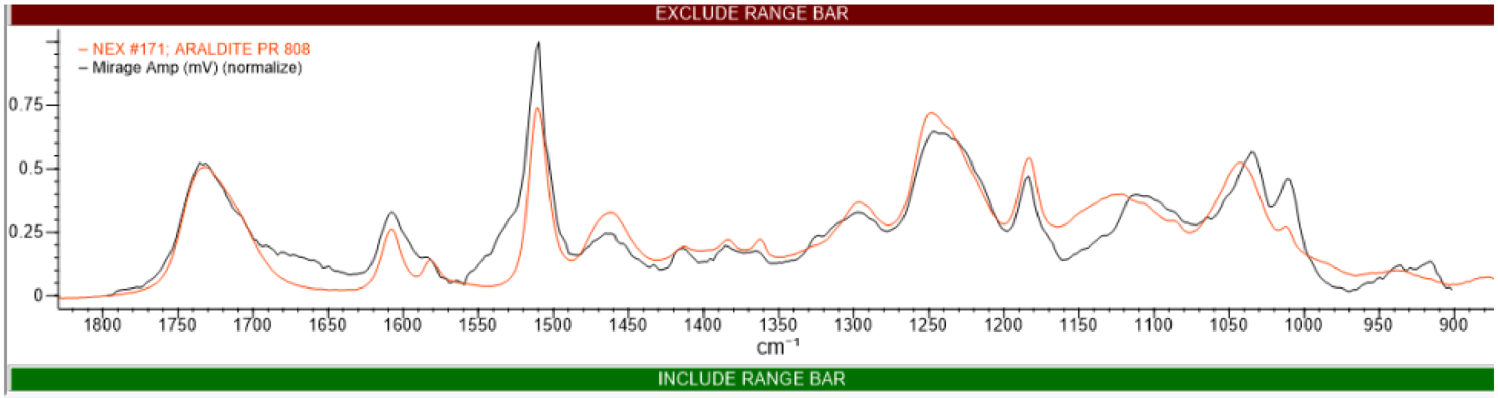
785 nm visible laser was used.

RGB Overlay Imaging



- RGB overlay of mIRage single frequency images shown on previous slide. RGB image has been overlaid on the 40 x optical image.

KnowItAll IR database searching

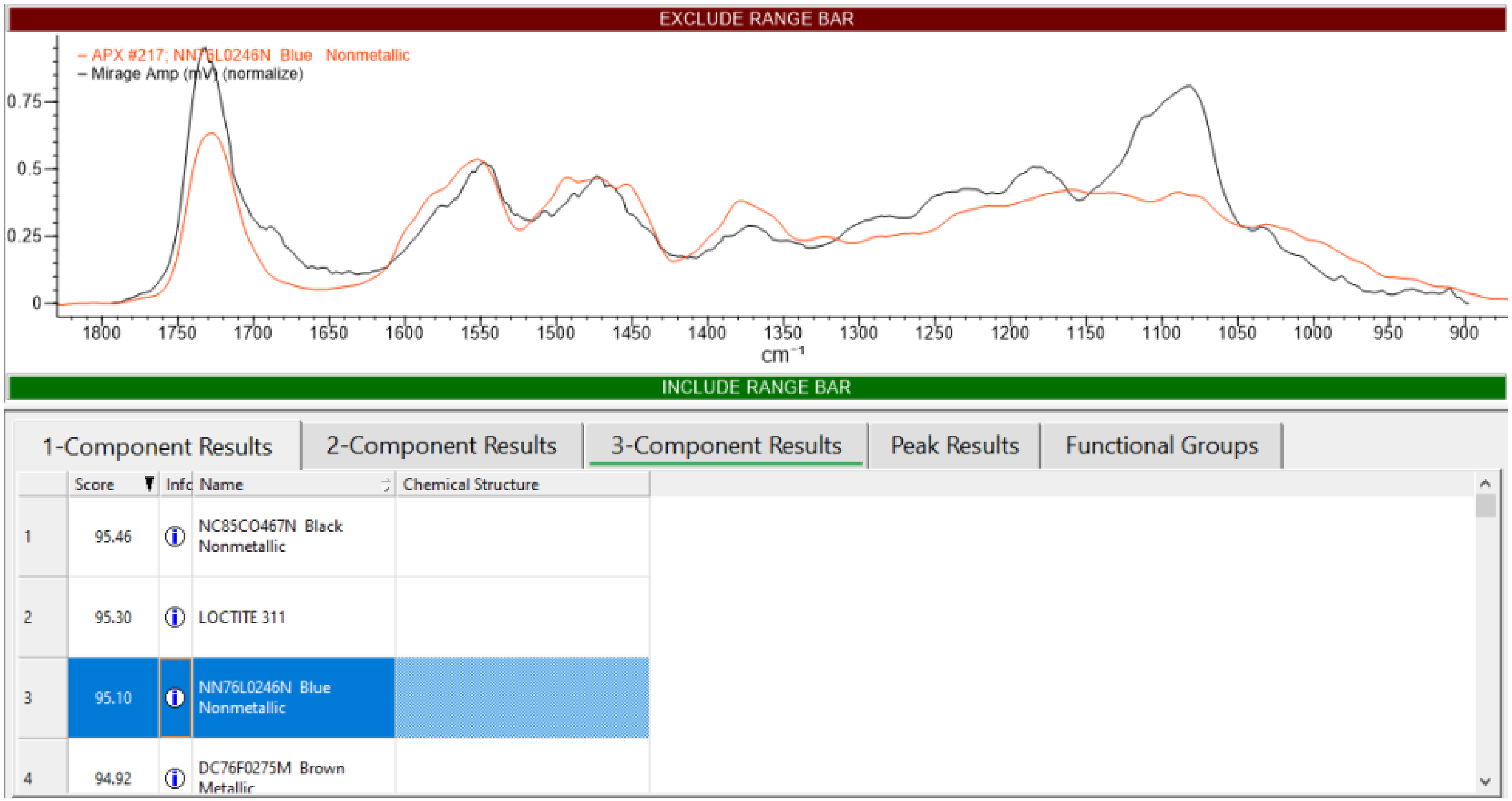


1-Component Results | 2-Component Results | Peak Results | Functional Groups

	Score	Info	Name	Chemical Structure
1	94.52	ⓘ	HELIOL 102-2	
2	93.70	ⓘ	ARALDITE PR 808	
3	93.07	ⓘ	THURANE	
4	92.72	ⓘ	TRA-BOND F 202 A/B (CURED)	

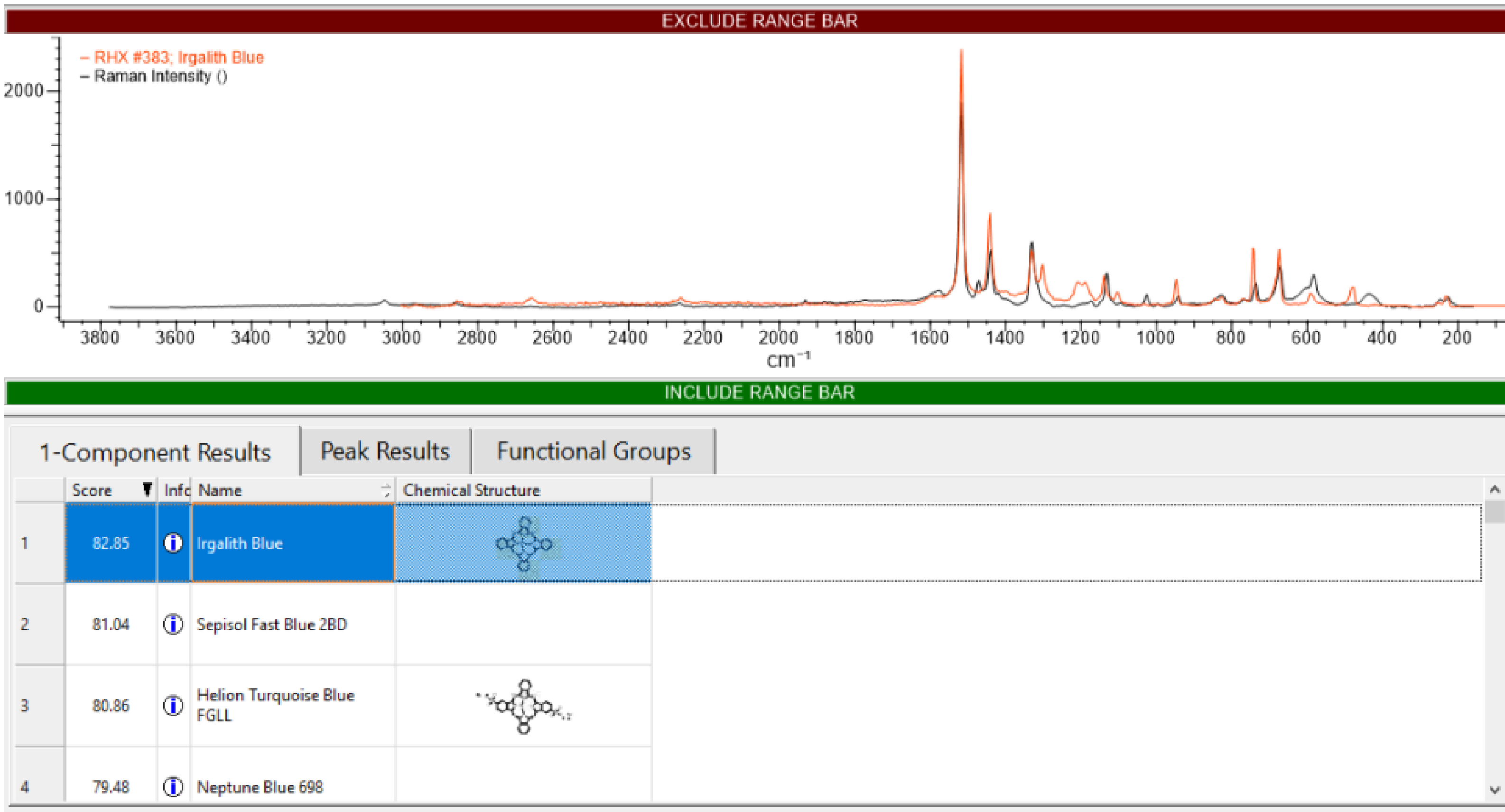
- KnowItAll IR data base searching of the outermost layer (red) suggests the material is Araldite, a water containing resin.

KnowItAll IR database searching

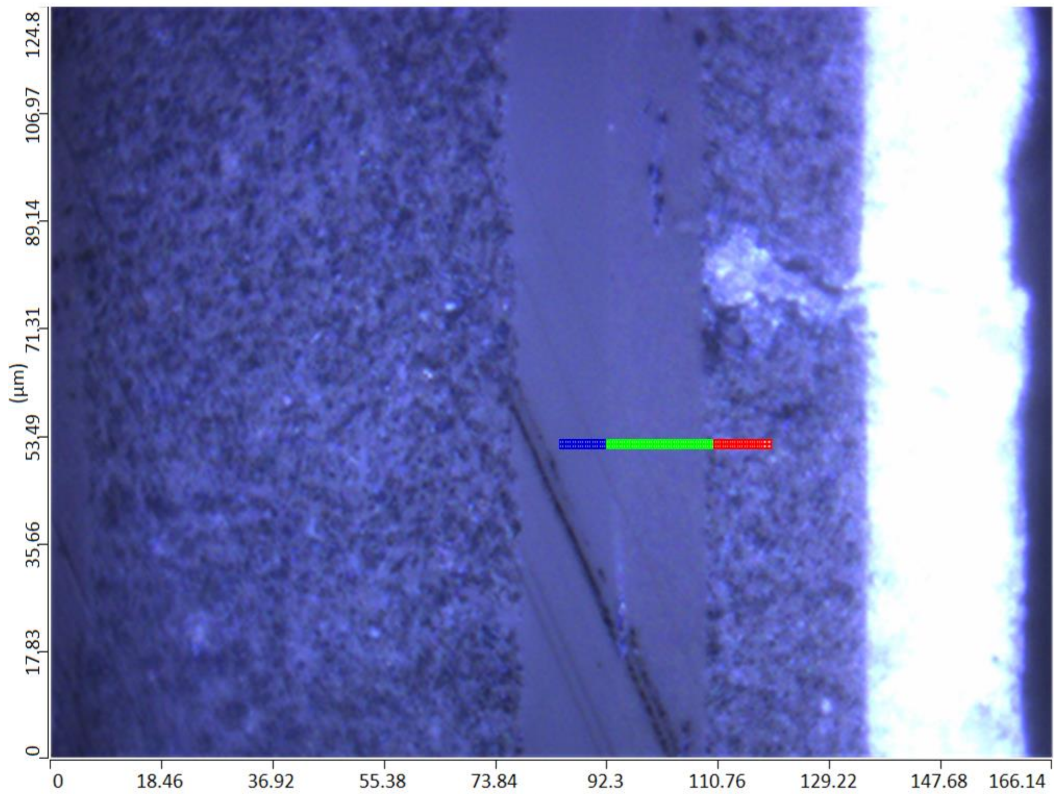


- KnowItAll IR data base searching of the layer (green) identifies the material as a Blue Nonmetalic paint chip using the IR Automobile paint chips database.

KnowItAll Raman database searching



Optical image of right side of sample D-1



mIRage 40x optical image

- Markers on image indicate the location of subsequent mIRage line array, data shown on next slide.

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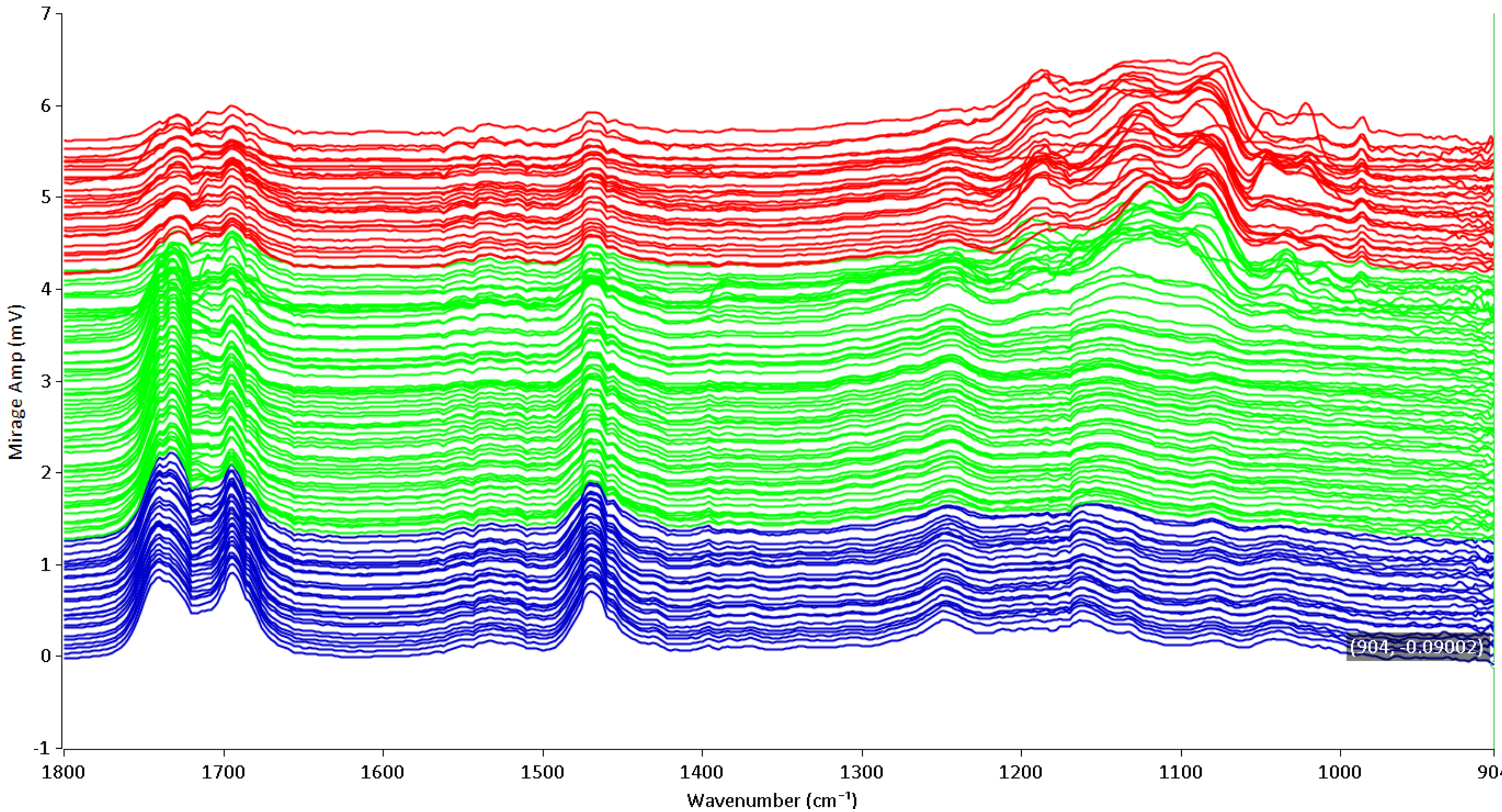
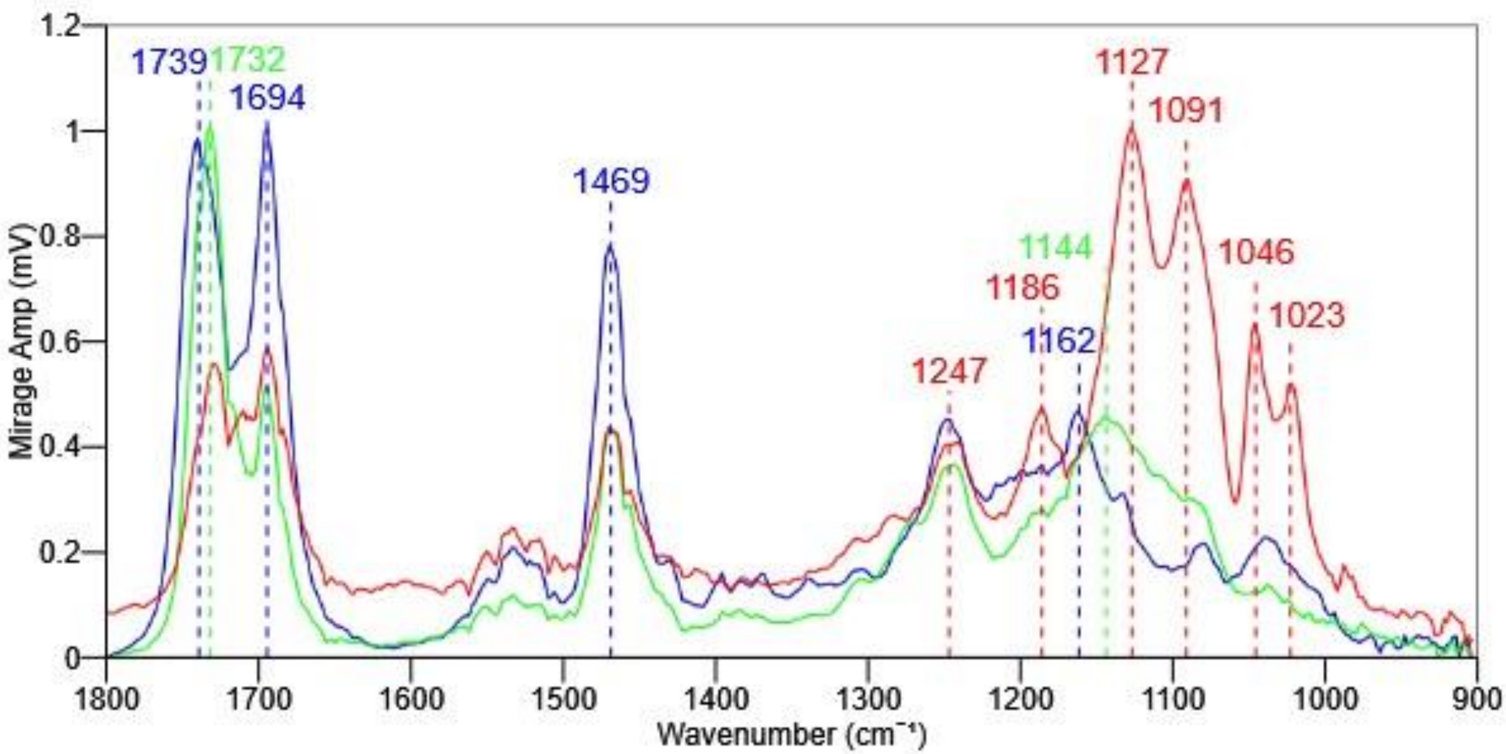
mIRage line array on sample D-1



- mIRage line array spectra, collected with 500 nm point spacing.

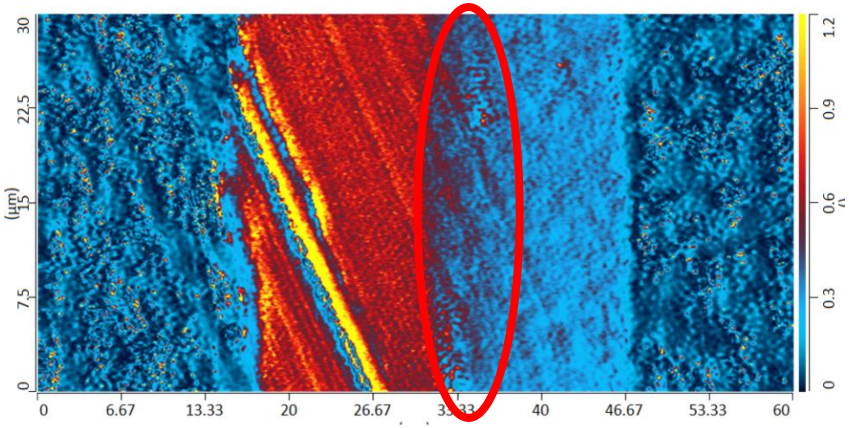
532 nm excitation laser was used. Data was collected with 500 nm spacing.

Selected spectra from each layer of sample D-1

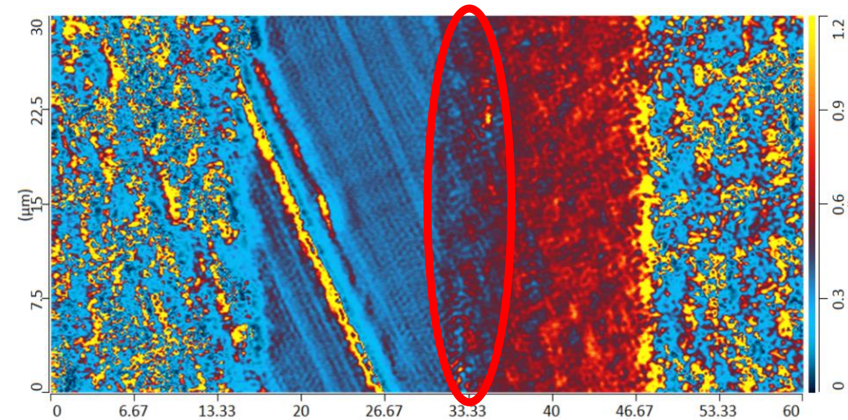


- Spectra shown above are selected from the line array on the previous slide as representative of each layer. Spectra have been normalized to a constant value of 1.

mIRage single frequency imaging

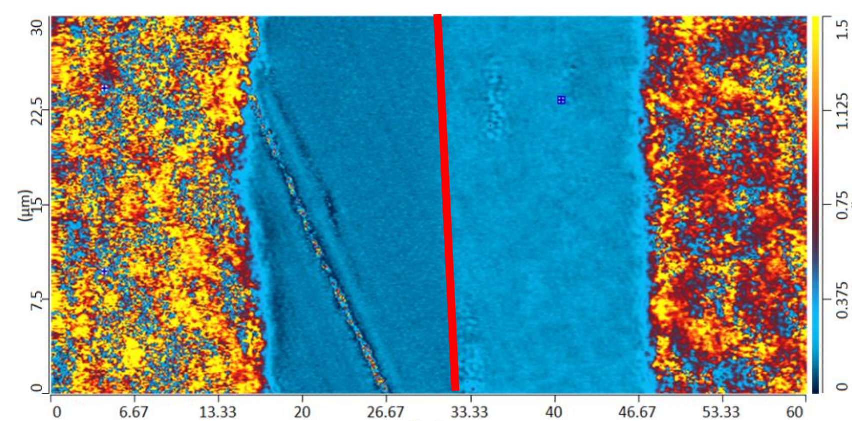


mIRage image ratio 1693/1730 cm^{-1}



mIRage image ratio 1730/1693 cm^{-1}

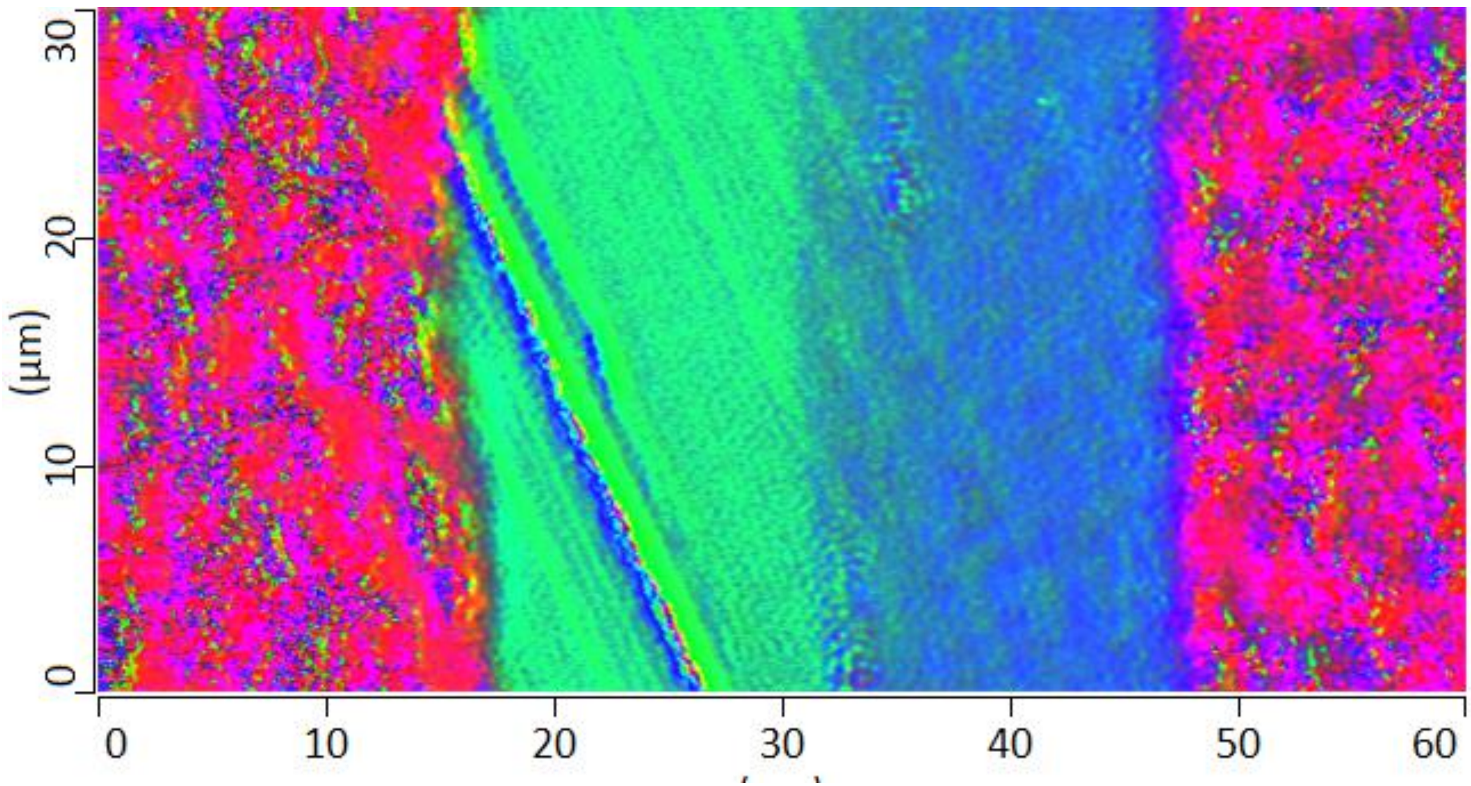
- mIRage ratio imaging highlights the various layers within the sample.
- Interestingly, there appears to be a roughly 2 µm region of mixing between the two interior layers.



mIRage image ratio 1091/1730 cm^{-1}

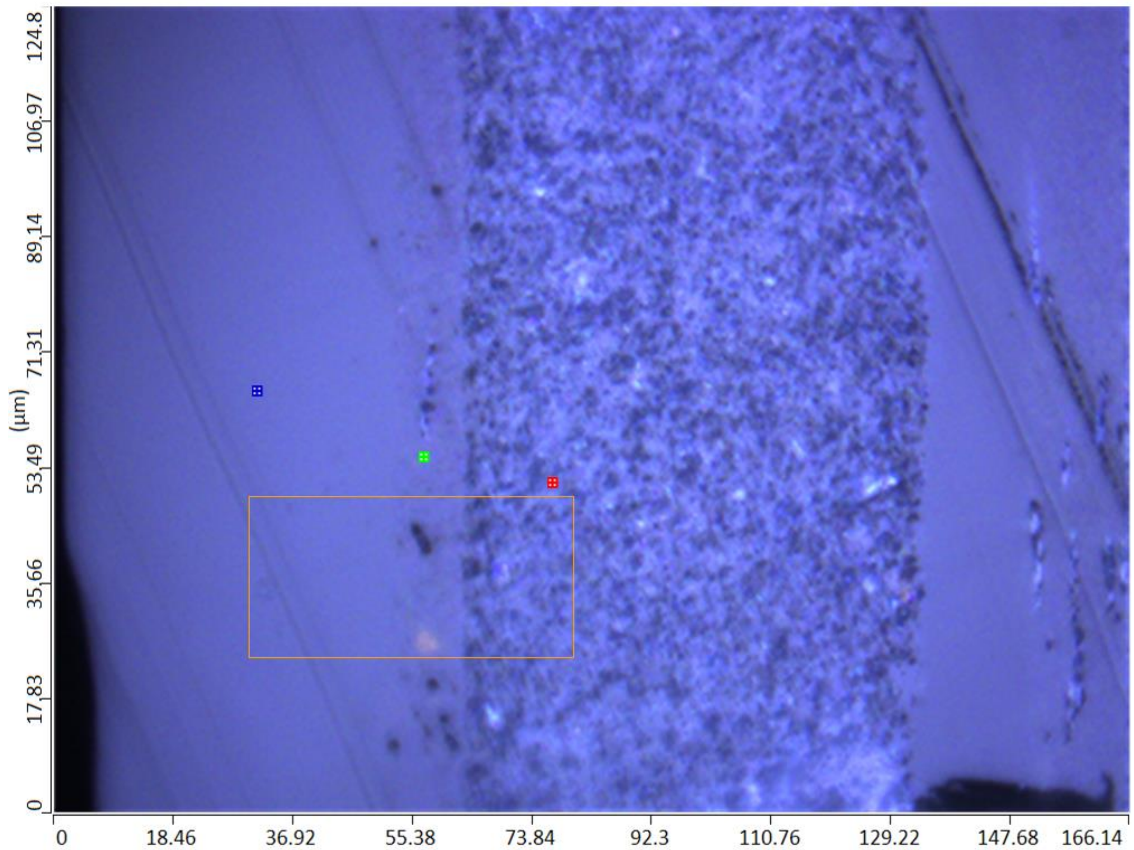
532 nm excitation laser was used. Data was with 100 nm point spacing

RGB overlay image



- RGB overlay of mIRage single frequency images shown on previous slide.

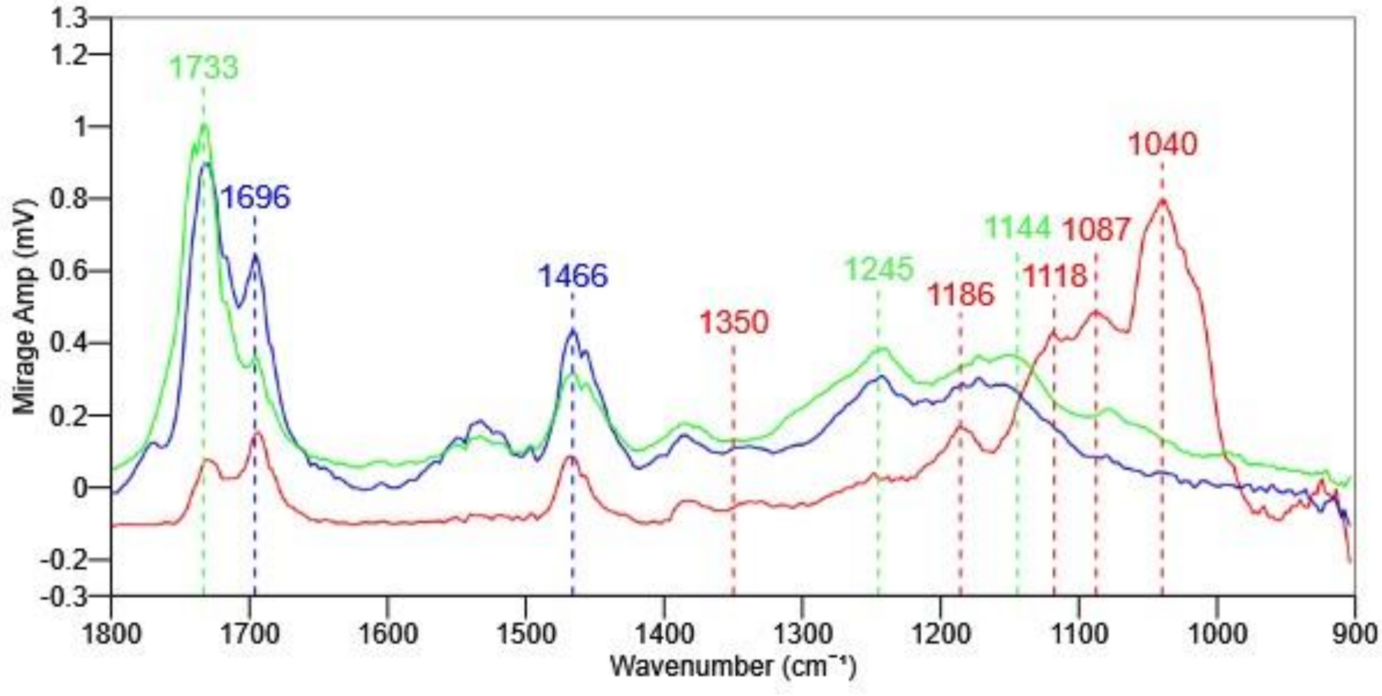
Optical image of left side of sample D-1



mIRage 40x optical image

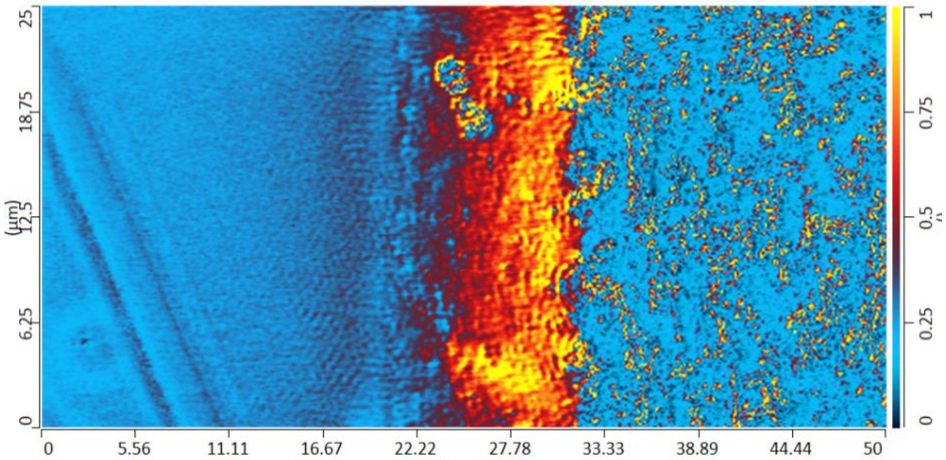
- Markers on image indicate the location of subsequent mIRage spectra.

mIRage QCL spectra from left side of sample D-1

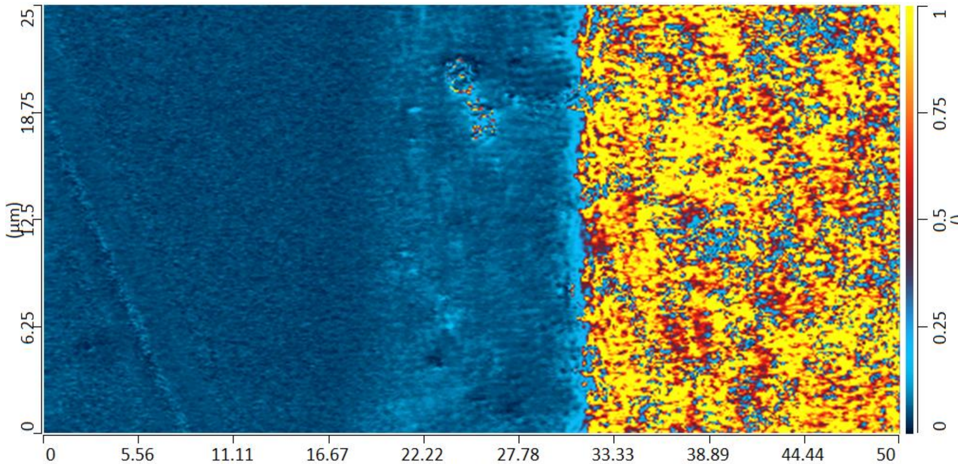


785 nm excitation laser was used..

mIRage single frequency imaging



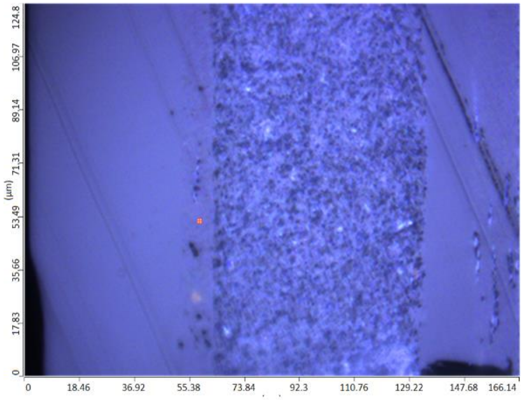
mIRage image ratio 1732/1693 cm^{-1}

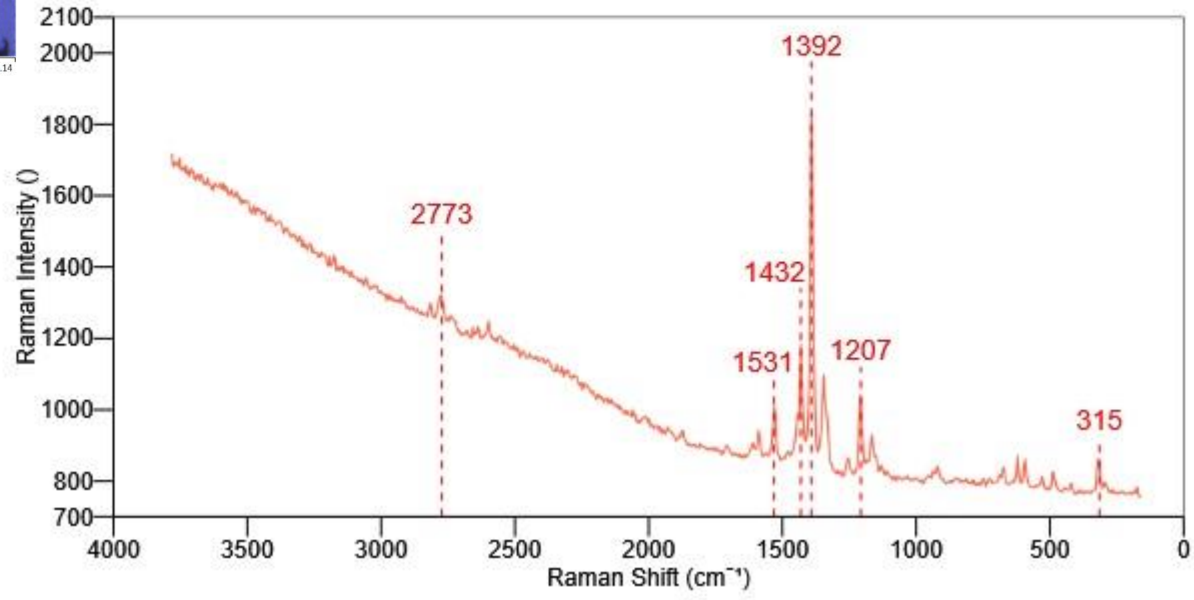


mIRage image ratio 1040/1732 cm^{-1}

785 nm excitation laser was used.

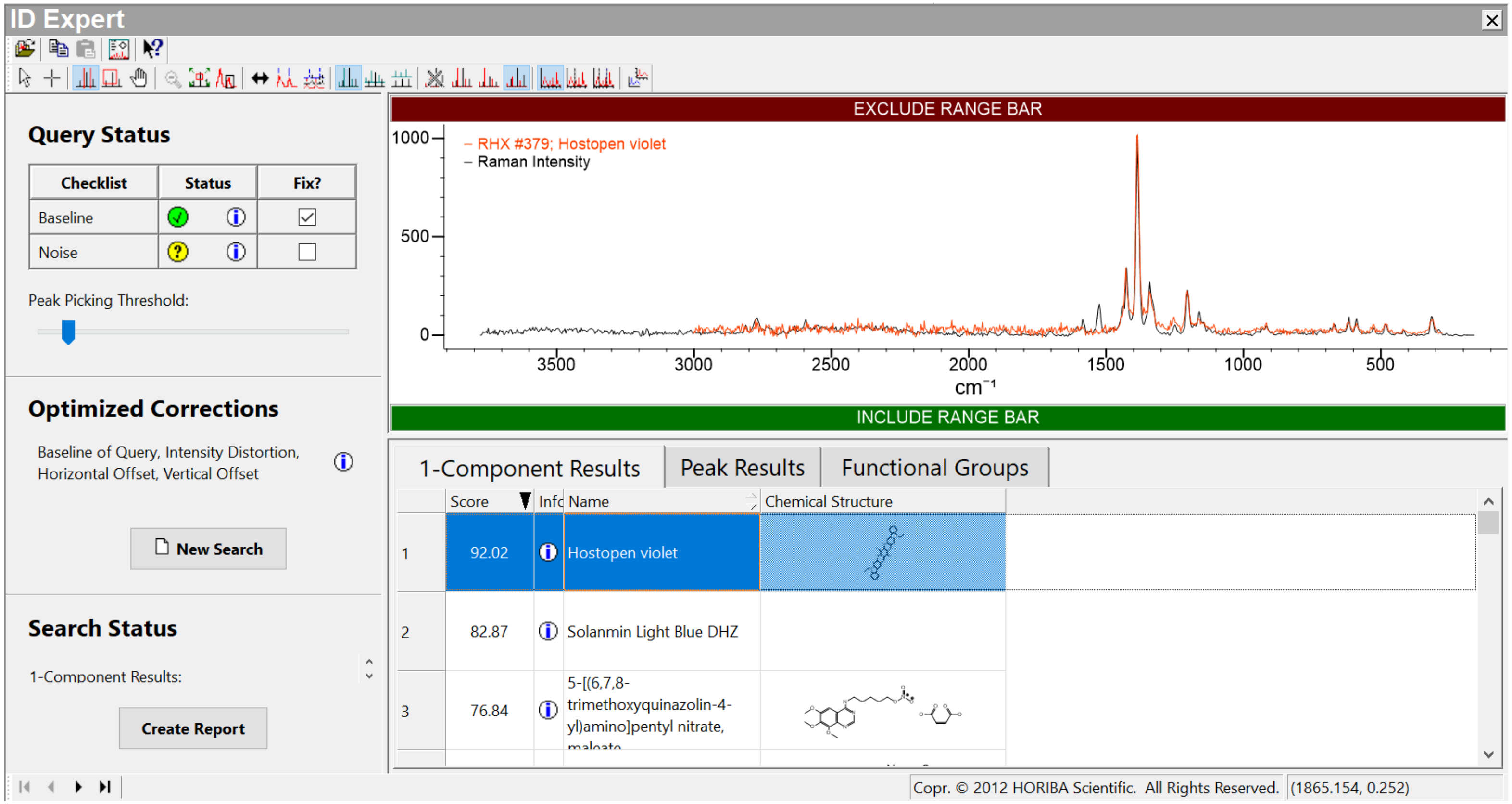
Raman spectrum from thinnest layer





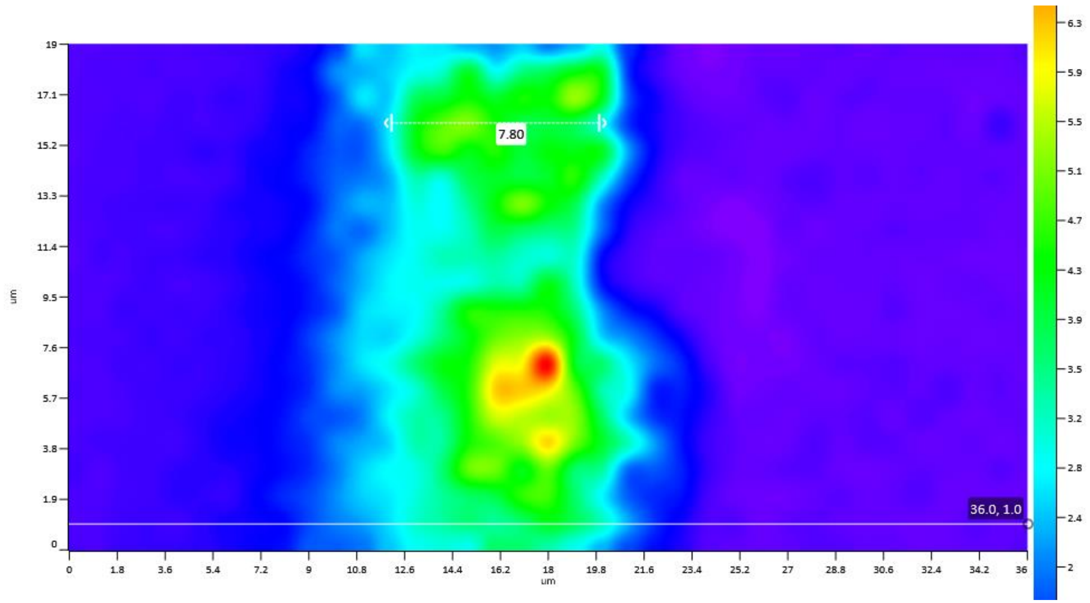
785 nm excitation laser was used.

KnowItAll Raman database searching



- KnowItAll Raman database searching identifies the thinnest layer within the sample as a violet dye material. The database used for spectral identification was the Horiba-Forensics Raman database.

Raman Hyperspectral image of pigment layer



- This Raman hyperspectral image displayed at 1392 cm^{-1} highlights the distribution of the pigment identified on the previous slide. Each pixel in this image has a complete Raman spectrum. Data was collected with a 785 nm laser and at 1 µm spacing in X and Y.

785 nm excitation laser was used.

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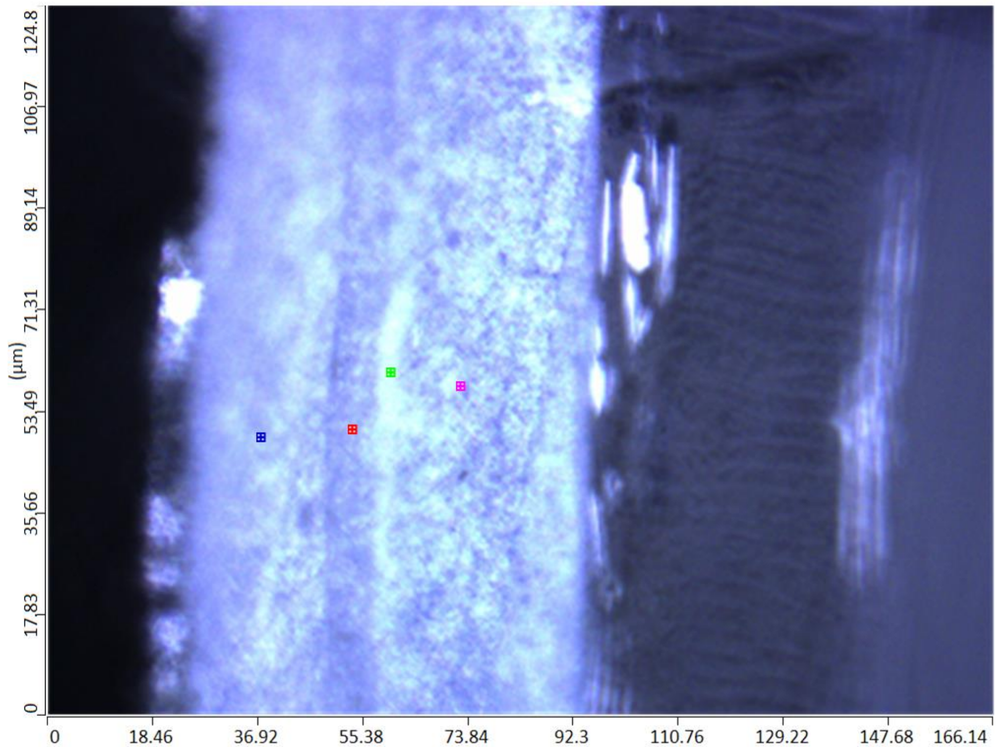
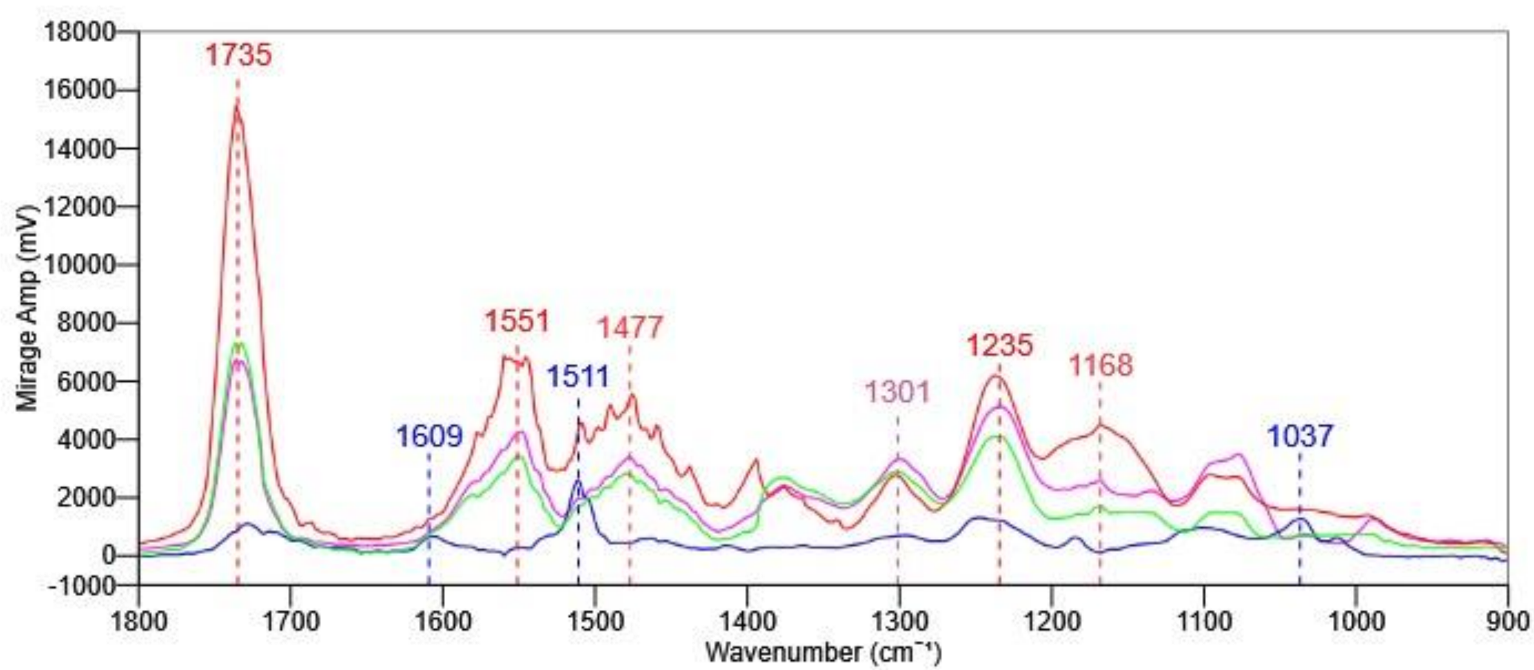
Optical image of left side of sample C-8



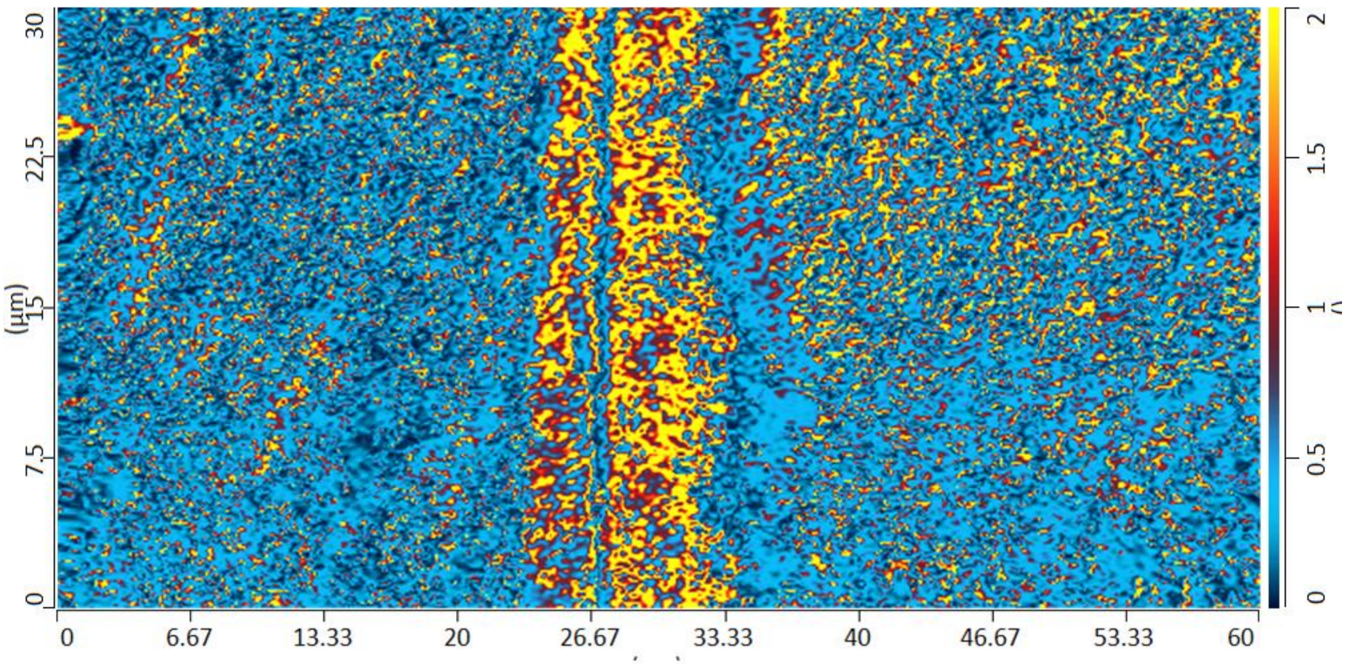
mIRage 40x optical image

- Markers on image indicate the location of subsequent mIRage spectra.

mIRage QCL spectra on left side of C-8



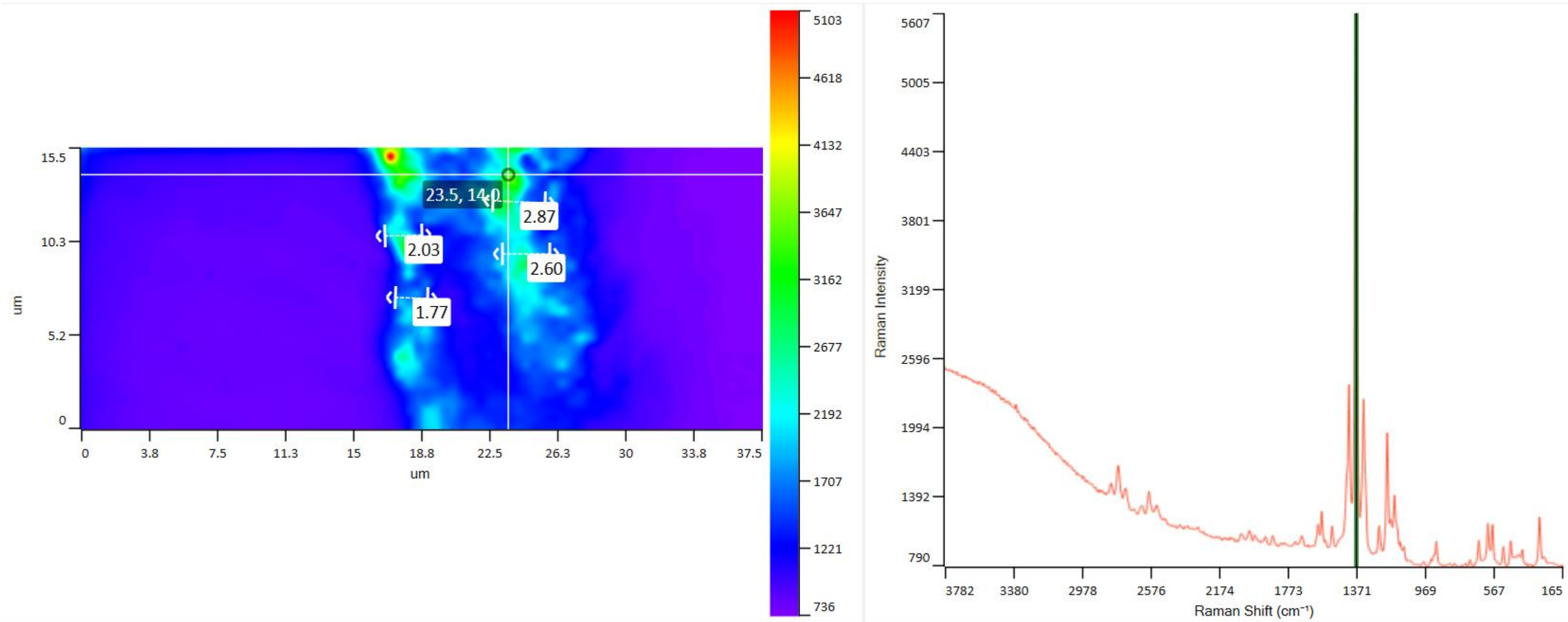
mIRage single frequency imaging



mIRage image ratio of 1730/1235 cm^{-1}

- Interestingly, the mIRage ratio image appears to show a layered structure within the center layers.

Raman hyperspectral on left side layers of C-8



- Similar to mIRage imaging, this Raman hyperspectral image (displayed at a Raman shift of 1376 cm^{-1}) also shows evidence of a thin layering structure within the center layers.
- These layers are measured to be roughly 2 µm each.

Data was collected with a 532 nm laser and at 500nm spacing in X and Y.

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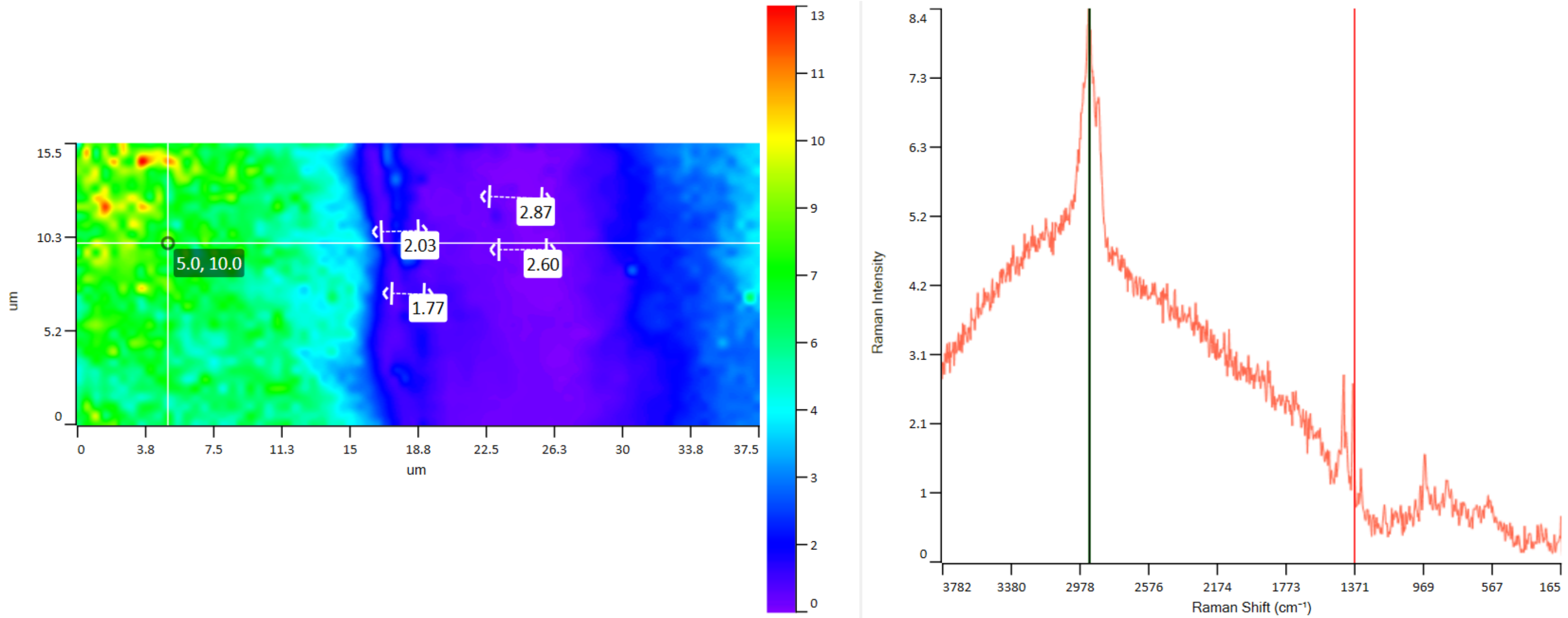
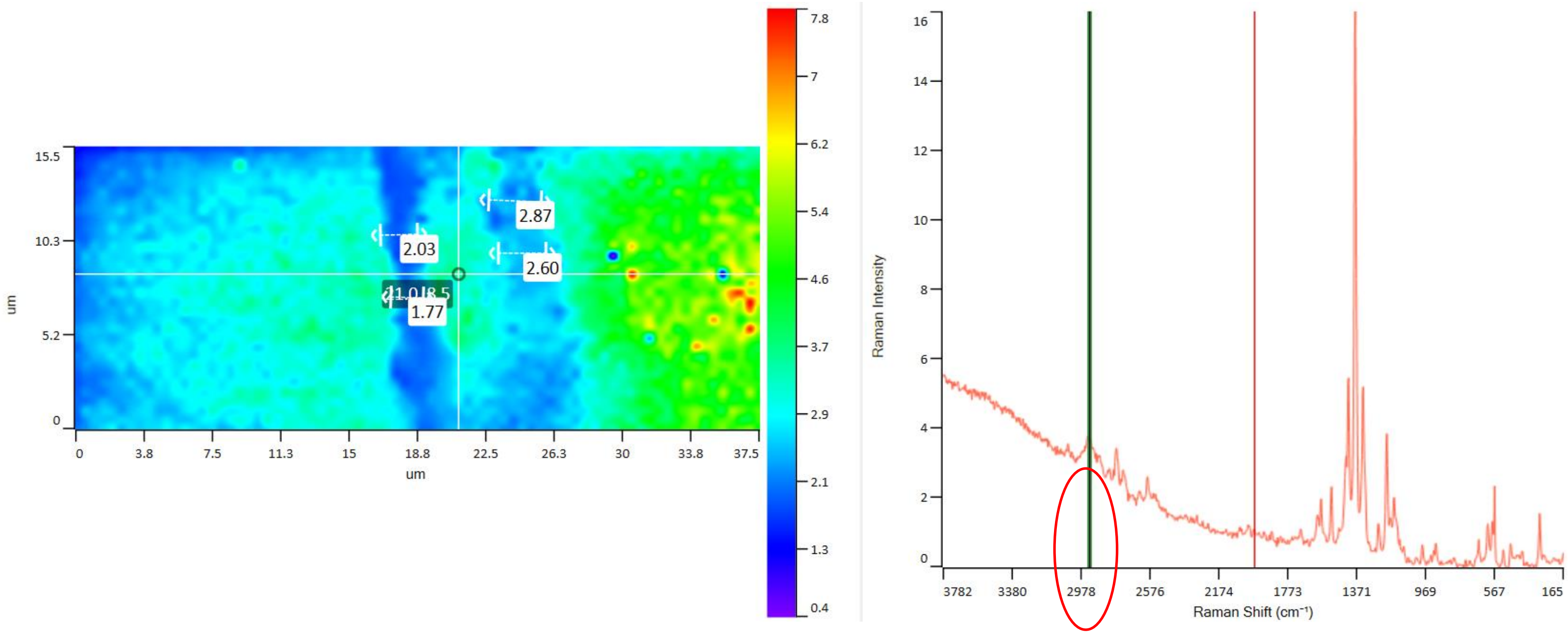
Raman hyperspectral on left side layers of C-8



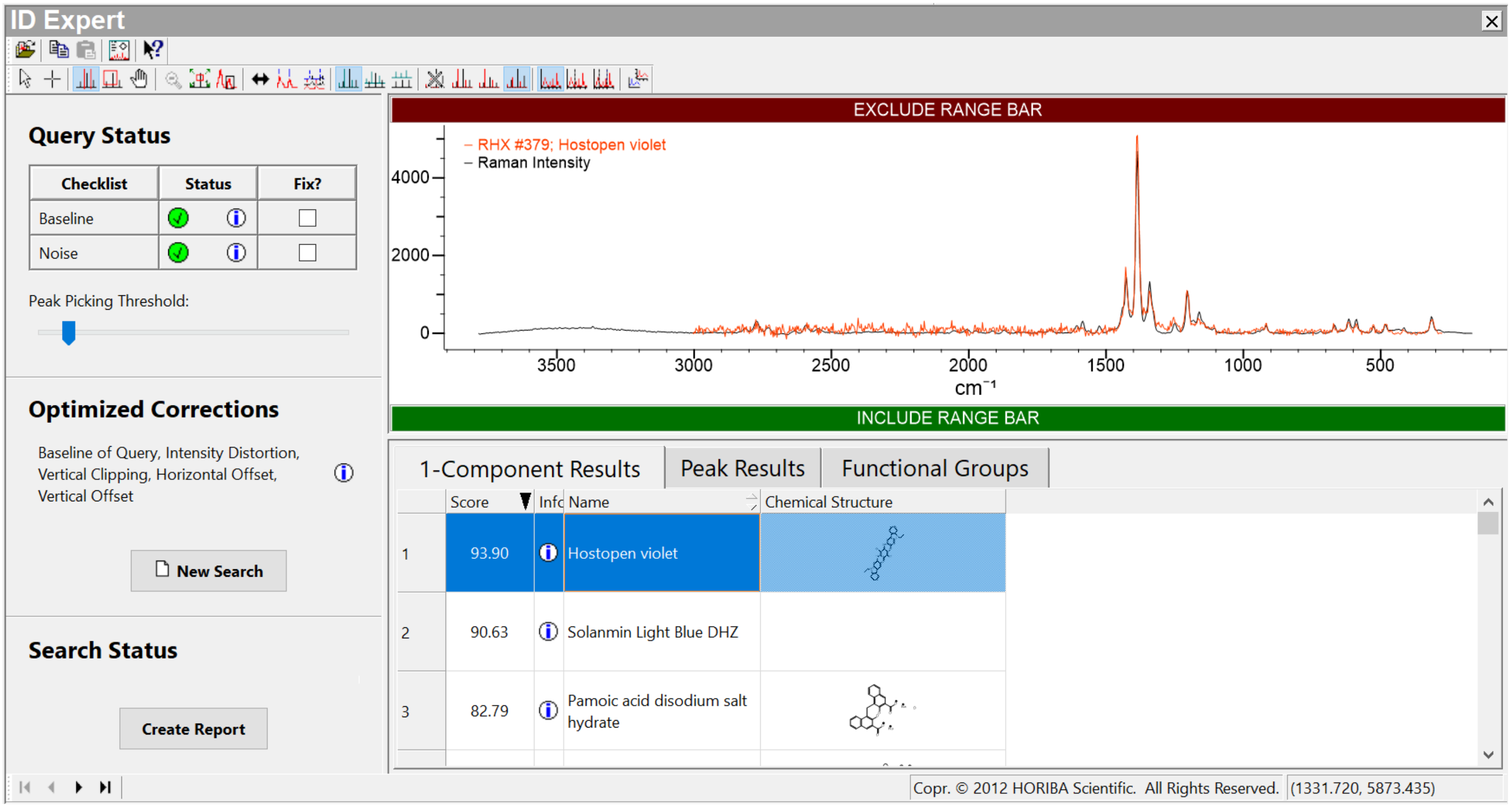
- This is the same hyperspectral data set as the previous slide, this time displayed at a Raman shift of 2926 cm^{-1}. The data has been normalized to 1376.

Raman hyperspectral on left side layers of C-8



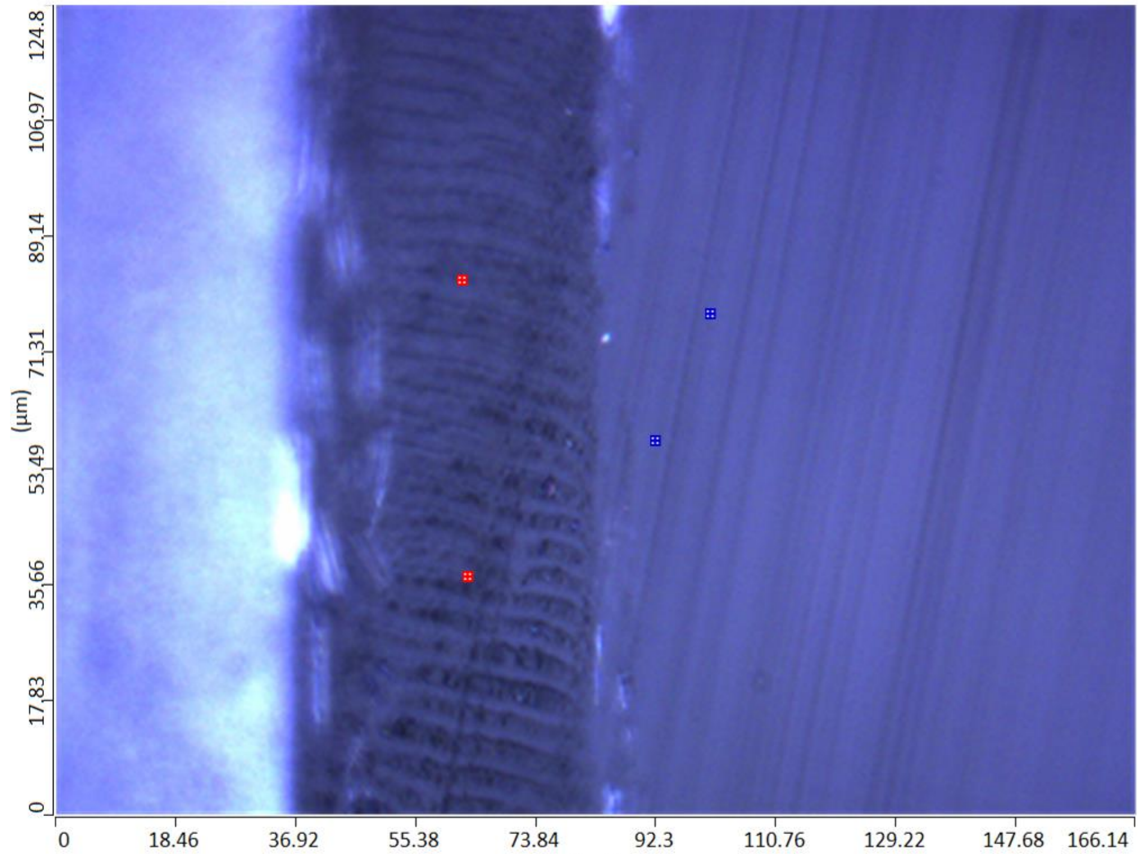
- Once again, this is the same hyperspectral data set as the previous slide, again displayed at a Raman shift of 2926 cm^{-1}. The data has been normalized to a baseline value.
- This data shows that the interior layer between the pigment layers shows a significant C-H peak (circled in red) when compared to surrounding pigment layers.

KnowItAll Raman database searching



- KnowItAll database searching interestingly shows a violet pigment. Visually, the paint has a silver color.

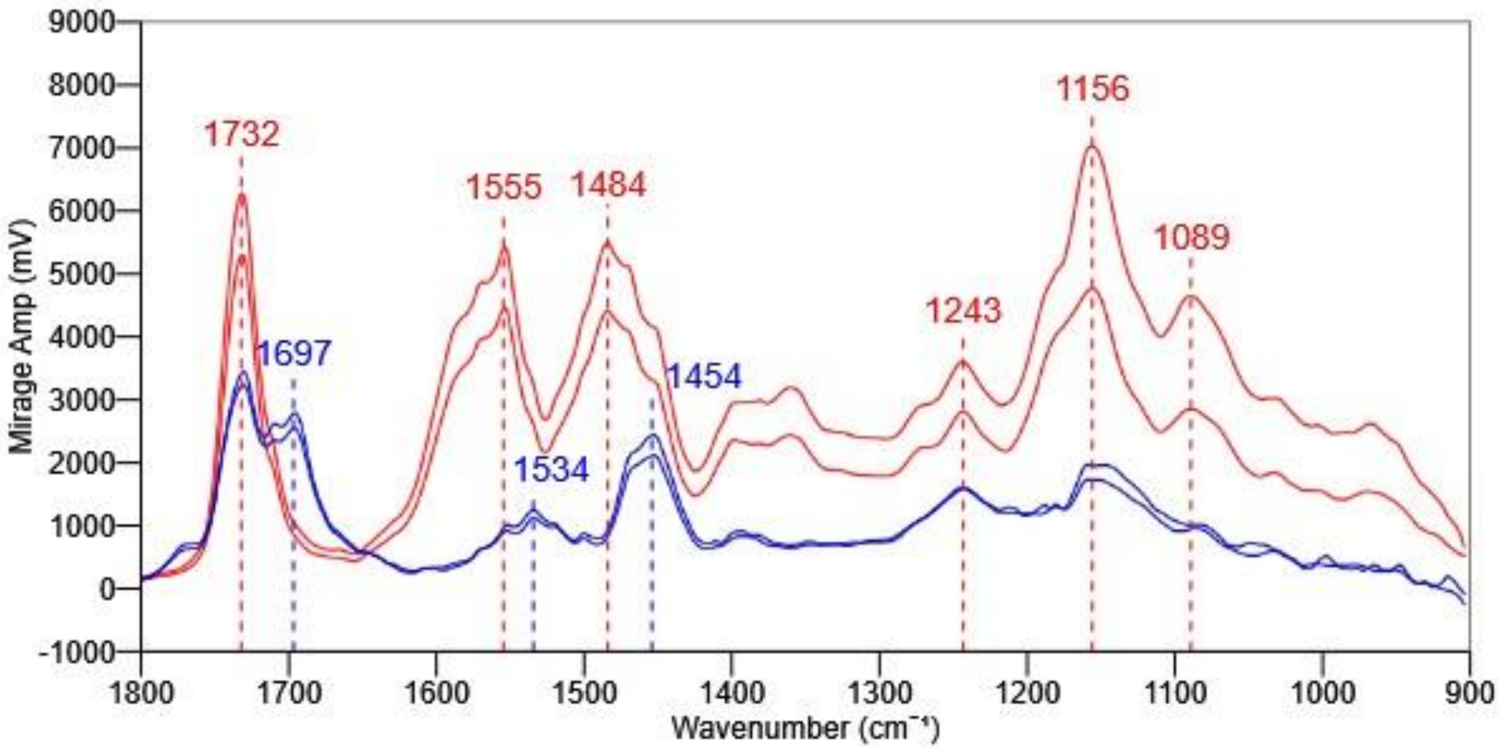
Optical Image of right side of Sample C-8



mIRage 40x optical image

- Markers on image indicate the location of subsequent mIRage spectra.

mIRage QCL spectra collected from right side of sample C-08



Data was collected with a 532 nm laser

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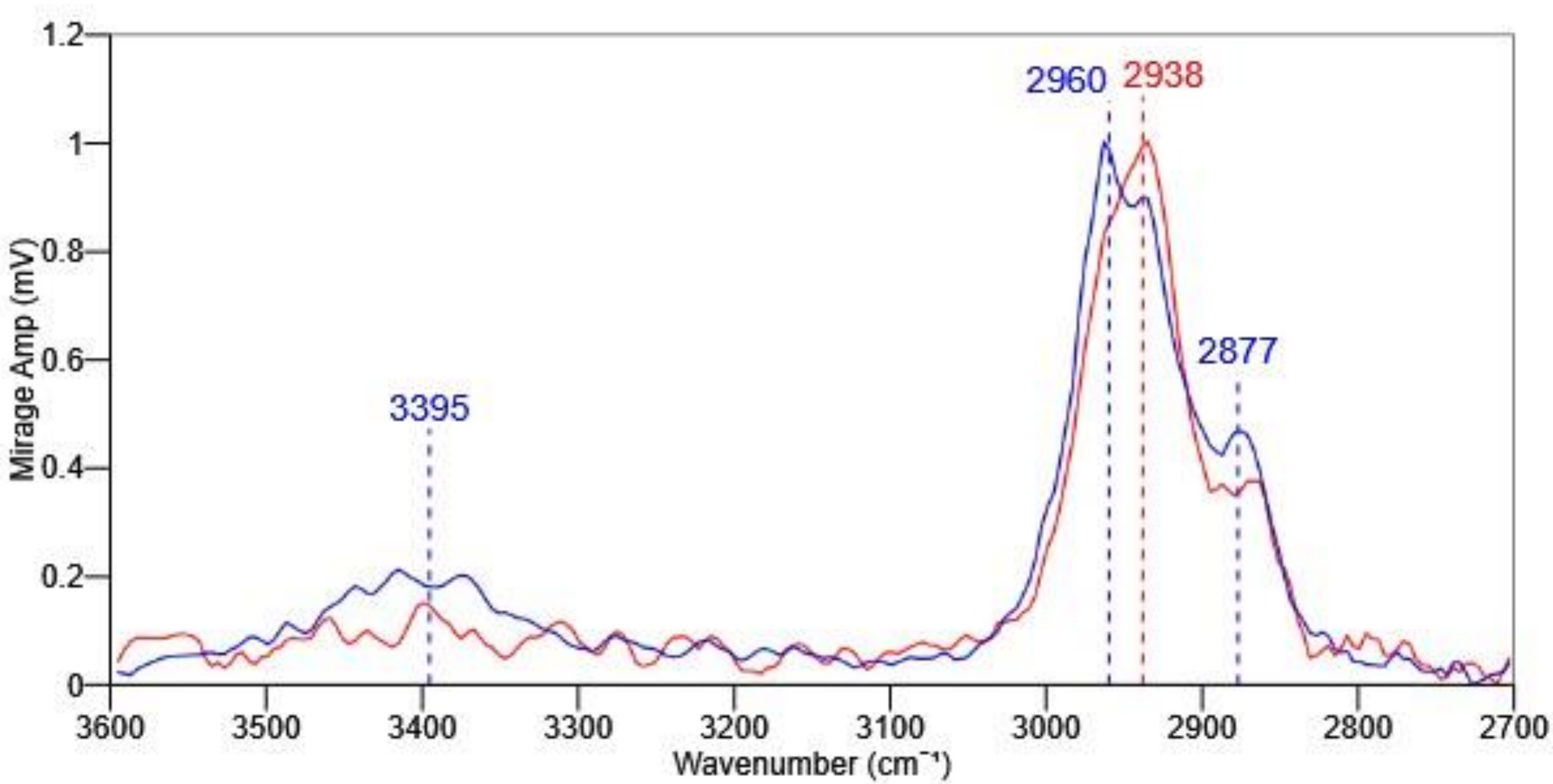
mIRage OPO spectra collected from right side of sample C-08



Data was collected with a 532 nm laser

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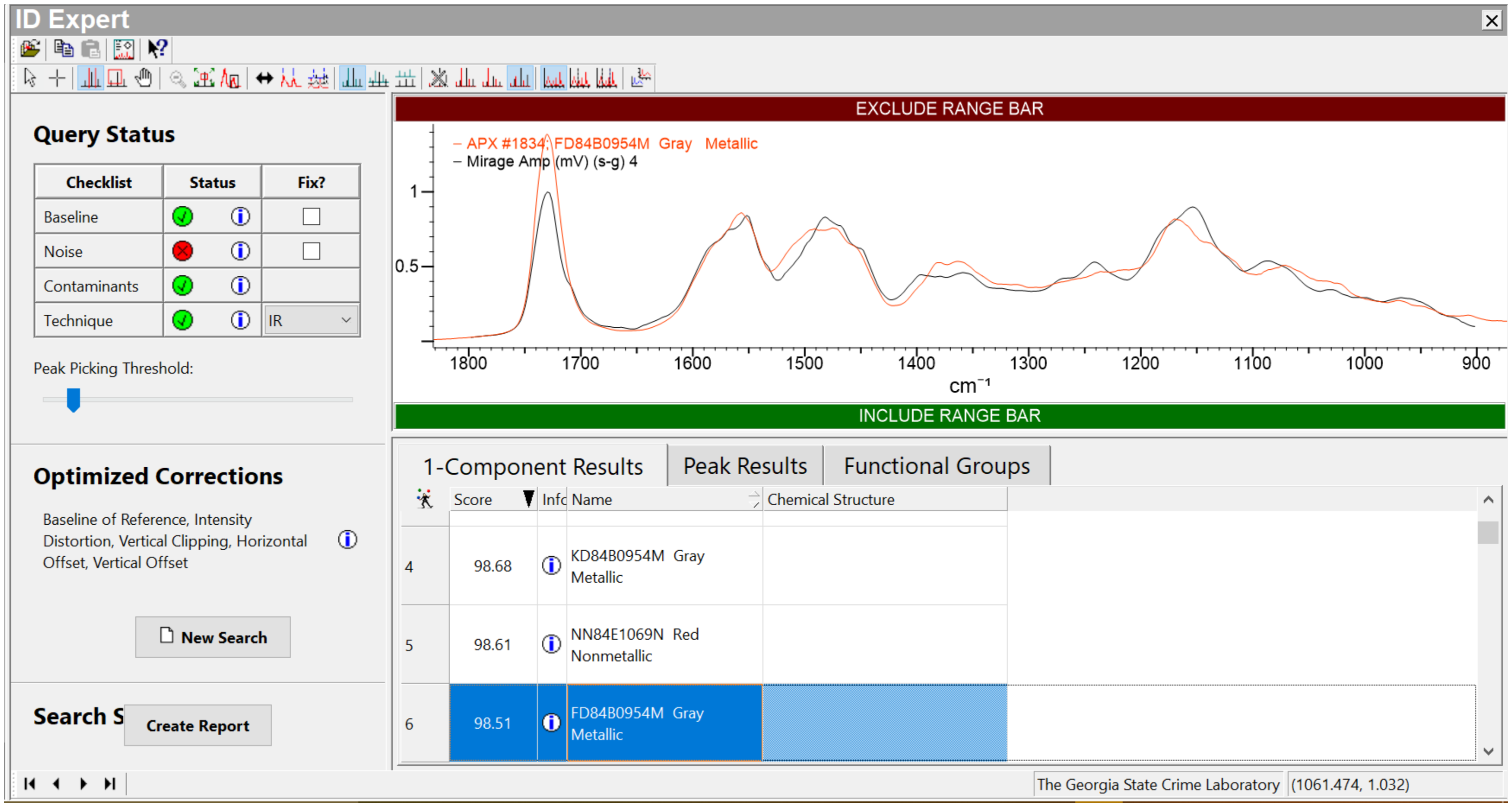
KnowItAll IR database searching



- KnowItAll database searching most likely identifies the material as a gray metallic automotive paint.

Conclusions

- The mIRage + R microscope uniquely enables the simultaneous Raman and IR characterization of a sample with limited sample preparation.
- The non contact regime ensures that no significant sample damages occurs, typically seen with ATR. Additionally, cross contamination issues are also eliminated.
- In this case, we have been able to identify multiple pigments (Blue and violet dyes) from Raman spectroscopy, using the KnowItAll spectral database. While IR spectra also result in database matches for paints.
- While Raman spectroscopy struggles with characterizing the binding material (due to fluorescence), mIRage excels.
- mIRage was able to collect IR spectra useful for characterizing the matrix material in pigment layers, as well as the purely organic layers.
- mIRage single frequency imaging and hyperspectral imaging shows the distribution of various chemical components along with layer boundaries, at high spatial resolution.