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Troubleshooting Spectral Results

Troubleshooting Spectral Results

Specular

Diffuse

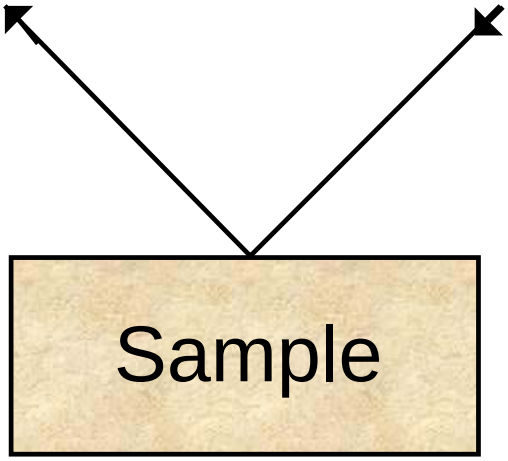
Scatter

Fringing

Water Vapor and Carbon Dioxide Correction

Specular Reflectance

- Low energy surface experiment
  (2-15% of Transmission)
- Little or no sample preparation
- Works well with samples with smooth surfaces



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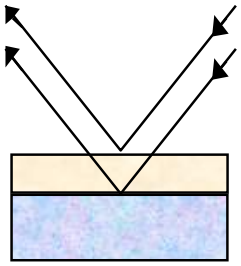
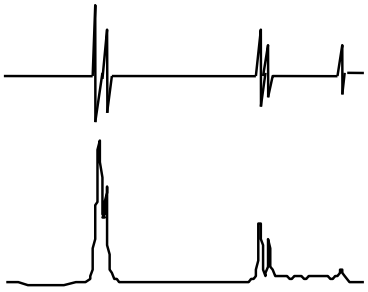
Specular reflectance experiments are non-destructive, easy, fast, require minimal sample preparation, and are quantifiable. This experiment is a surface technique, as this diagram suggests. The one requirement for successful collection is a flat, level surface. Inconsistencies in the surface structure will cause the energy to scatter which may make the interpretation of the data more difficult if not impossible.

Experimental Results
Combination



True specular component



Mixed Result

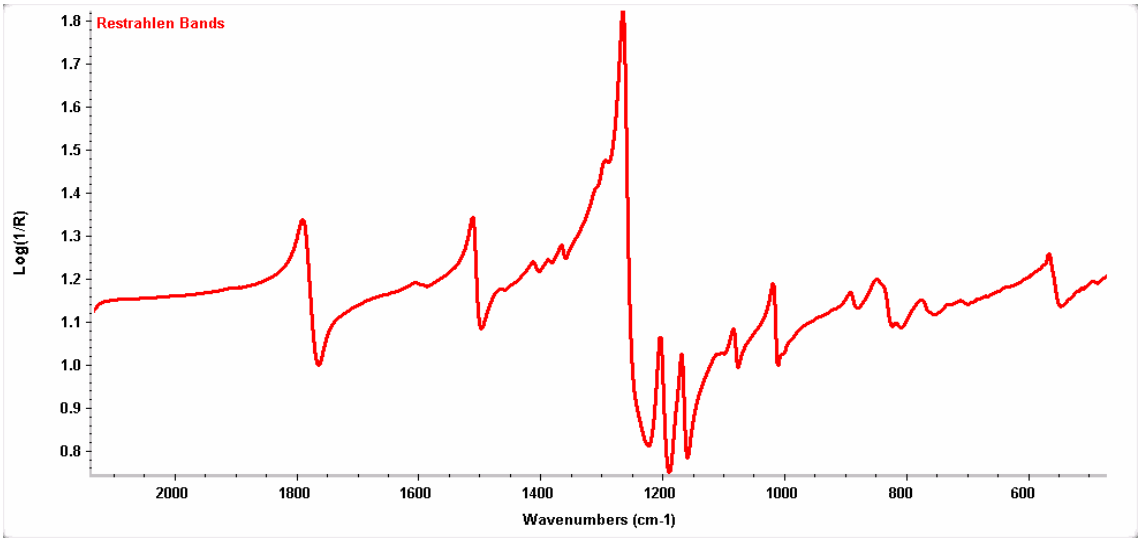
Reflection-Absorption component

Dependent on Sample Surface and Sample Thickness

Depending on the thickness of the coating it is possible to get a combination spectrum. The absorption information from the reflection-absorption interaction and the specular information from the reflection off the surface. If this happens Kramers-Kronig correction may distort the spectrum and the result may be useless. A different technique may be required.

Experimental Results
Specular Reflection

Uncorrected Restrahlen Bands



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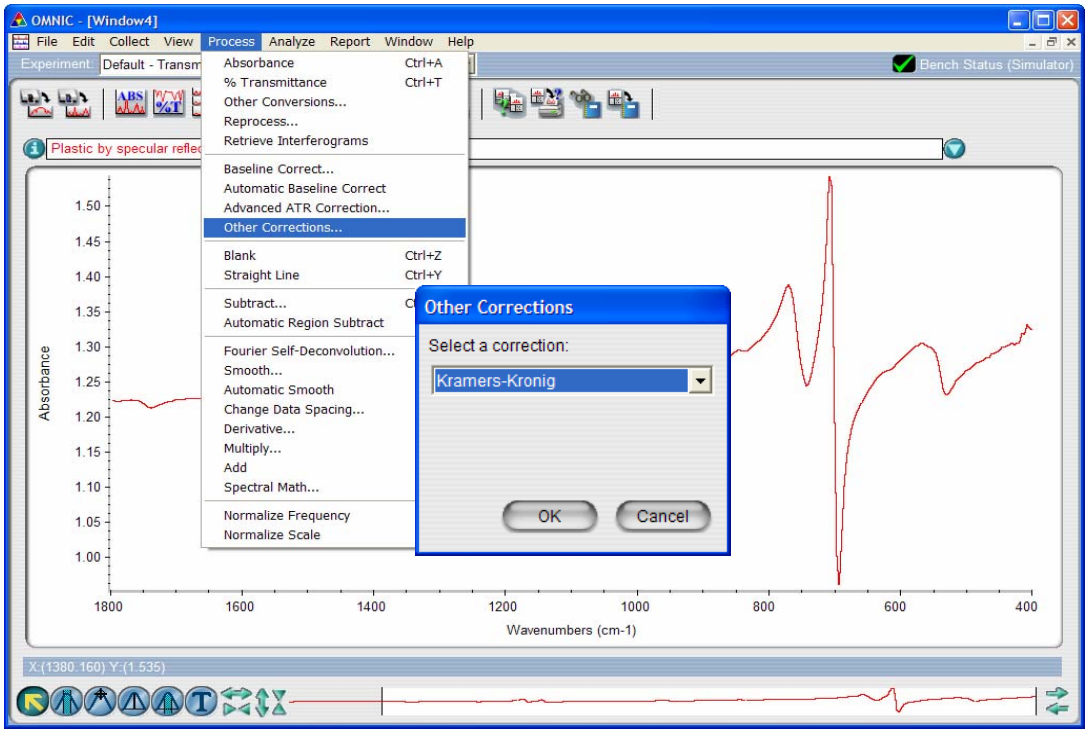
With pure reflectance experiments it is not uncommon to see derivative peaks in the spectrum. These derivative peaks occur because the refractive index changes in the absorption region of the molecular interaction. In order to qualitatively analyze the reflection data, a mathematical correction is performed that transforms the data to a form that is similar to transmittance data. In OMNIC this correction is the Kramers-Kronig correction.

For quantitative analysis the goal of the experiment is reproducibility. The reproducibility of this experiment is dependent on the surface of the sample. An inconsistent surface will produce inconsistent data.

Kramers-Kronig



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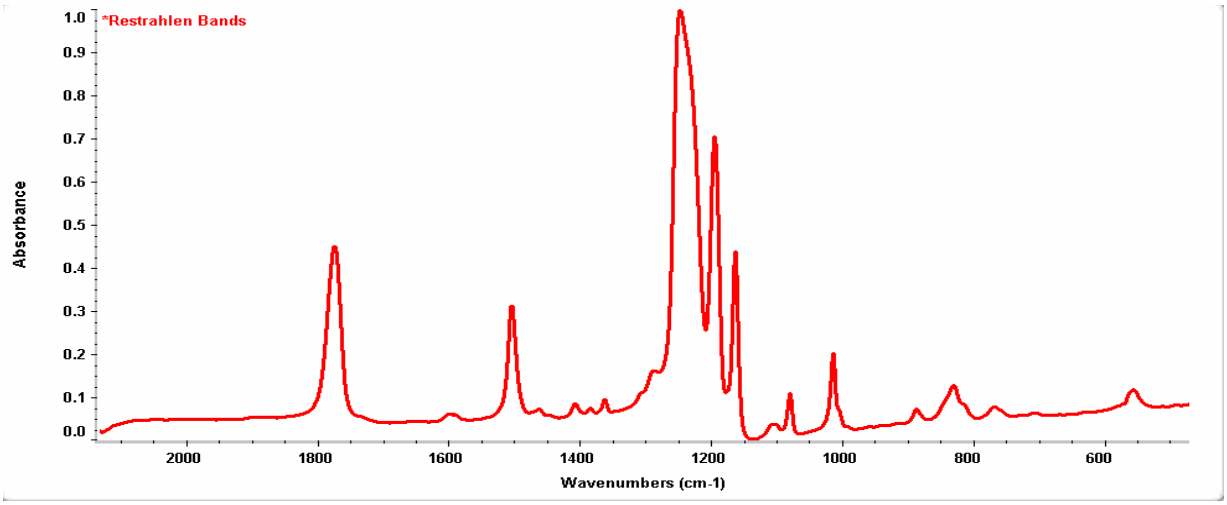
Kramers Kronig

Select

Process | Other Corrections | Kramers Kronig

It is very important to understand that Kramers Kronig should ONLY be used to correct data KNOWN to contain a specular component. Only data collected using a reflection technique can contain a specular component. If you have negative peaks and the data was collected with another analysis technique then there are other factors that may account for the appearance of the data.

Kramers-Kronig Correction



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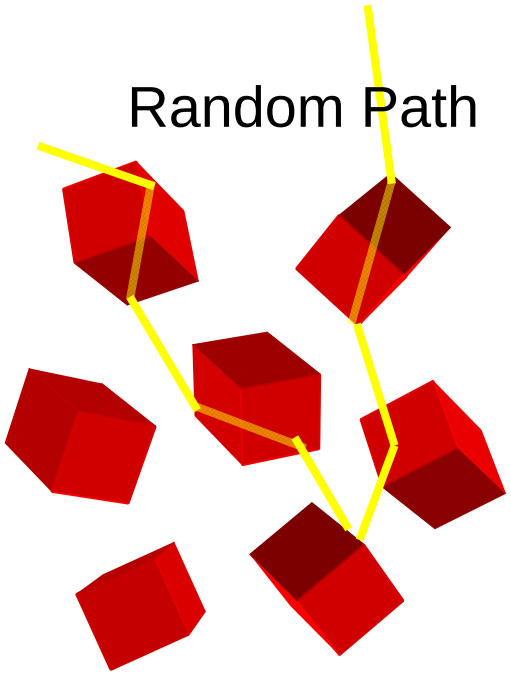
This is the same spectrum shown in the preceding pages after the Kramers-Kronig correction was applied.

Diffuse Reflectance

- Analyzes scattered energy
- Typically uses a support matrix, scattering agent like KBr
- Great for powders, grind to 5μm or less
- Collection of both reflectance and transmittance data



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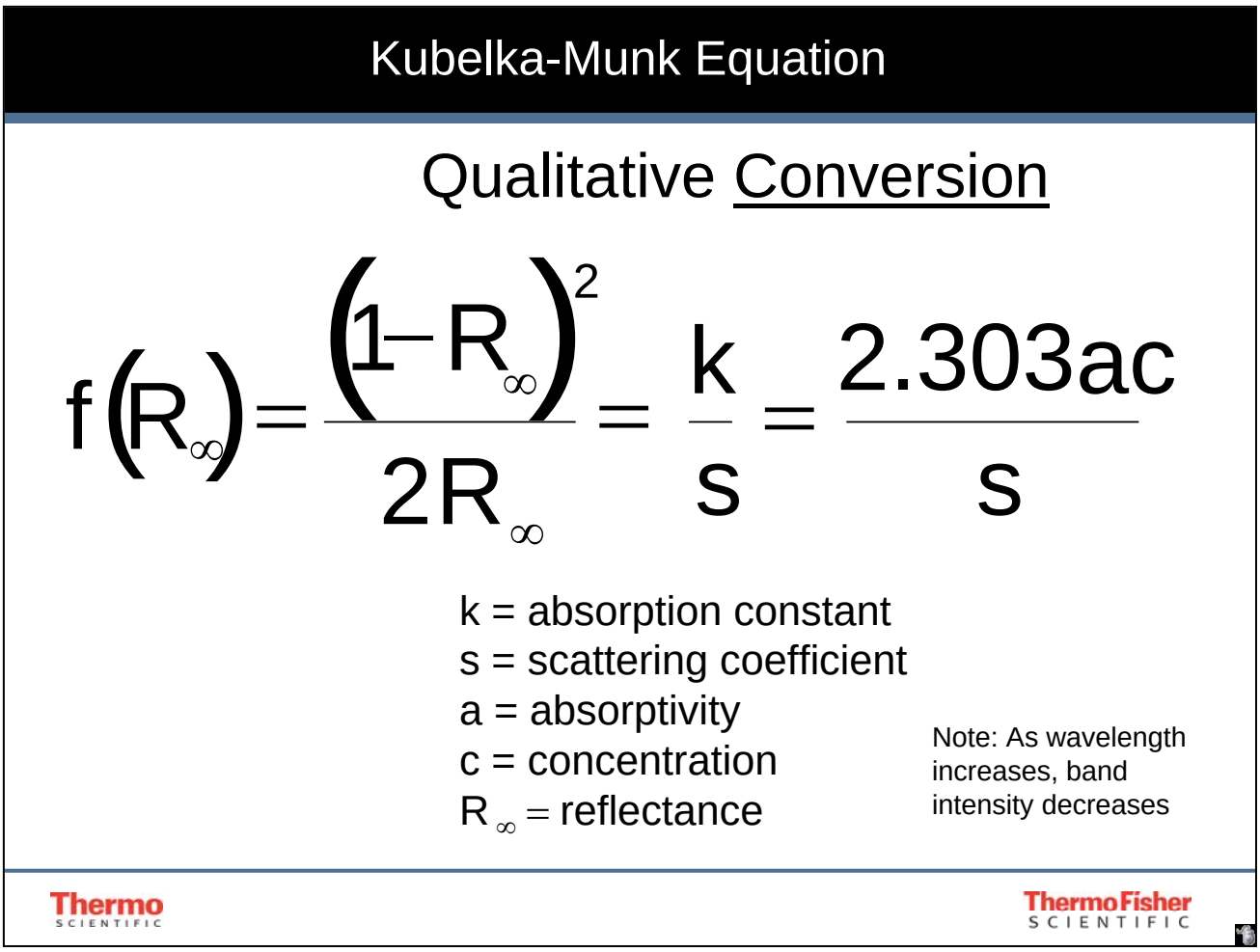
Diffuse Reflectance - Overview

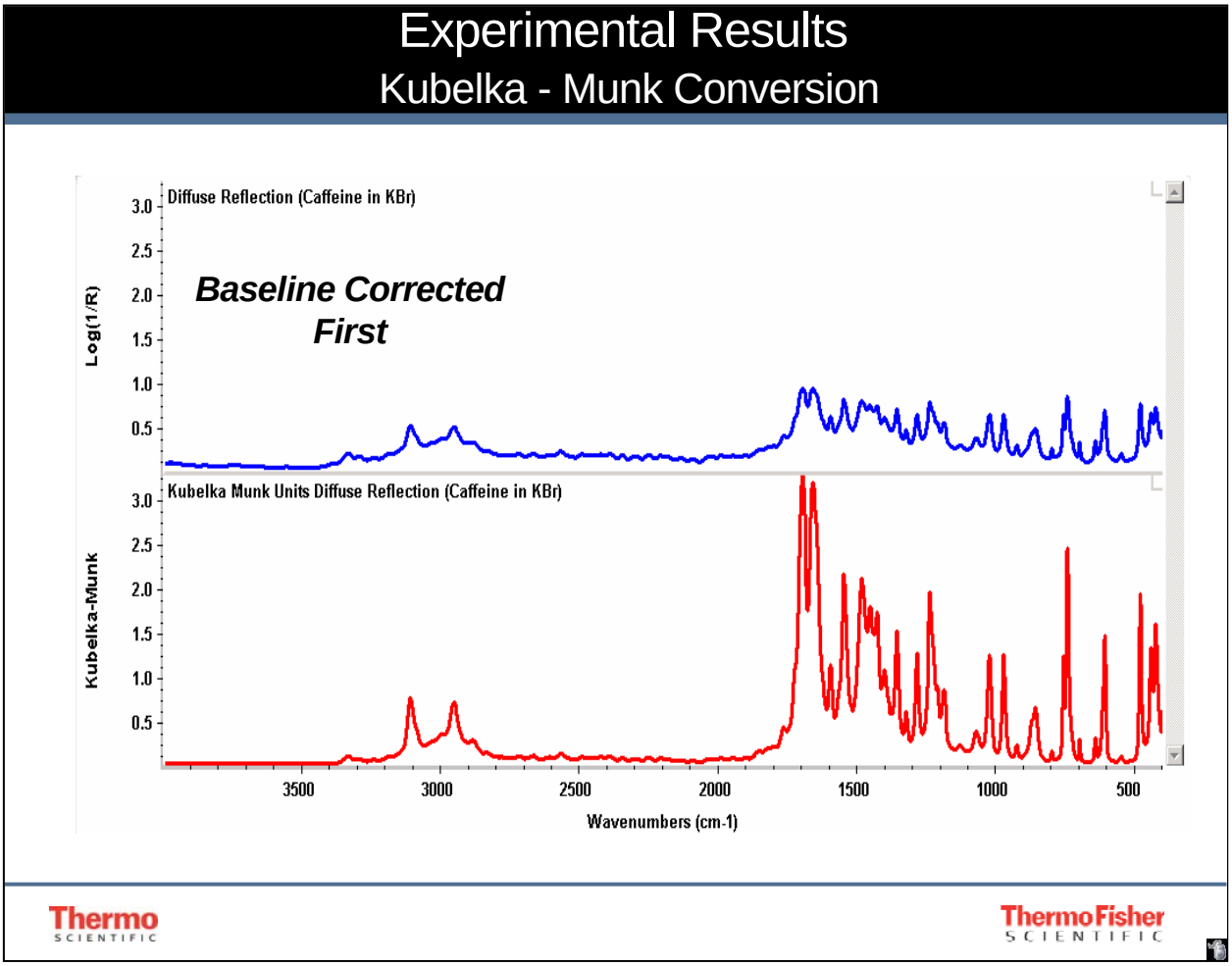
Diffuse reflectance infrared Fourier transform spectroscopy, DRIFTS, is a technique that collects and analyzes scattered energy. The sample, usually a powder, is mixed with a scattering agent like KBr. When the energy enters the sample it can either be reflected off the surface or be transmitted through one of the particles. The energy reflecting off the surface is typically lost. The energy that is transmitted through a particle can either reflect off the next particle or be transmitted through the second particle. In this way the energy comes in contact with the sample many times which increases the pathlength. In order to collect the sample information a spherical mirror is used to focus the scattered energy that comes from the sample onto the detector.



Kubelka - Munk Equation

It has been found that the intensities of the bands are dependent on the wavelength. As the wavelength increases (becomes longer) the intensities of the bands decrease relative to a pure transmission spectrum. Kubelka-Munk units were developed to take into account the fact that the band intensities of the diffuse reflectance spectrum are proportional to the concentration and the molar absorptivity, but inversely proportional to the scattering coefficient. The Kubelka-Munk units are used for qualitative comparisons with absorbance units.

This scale is useful in comparing spectra from transmission libraries with data collected in diffuse reflection. Overlay and direct comparisons are made easier if the diffuse data is displayed in the Kubelka-Munk units.

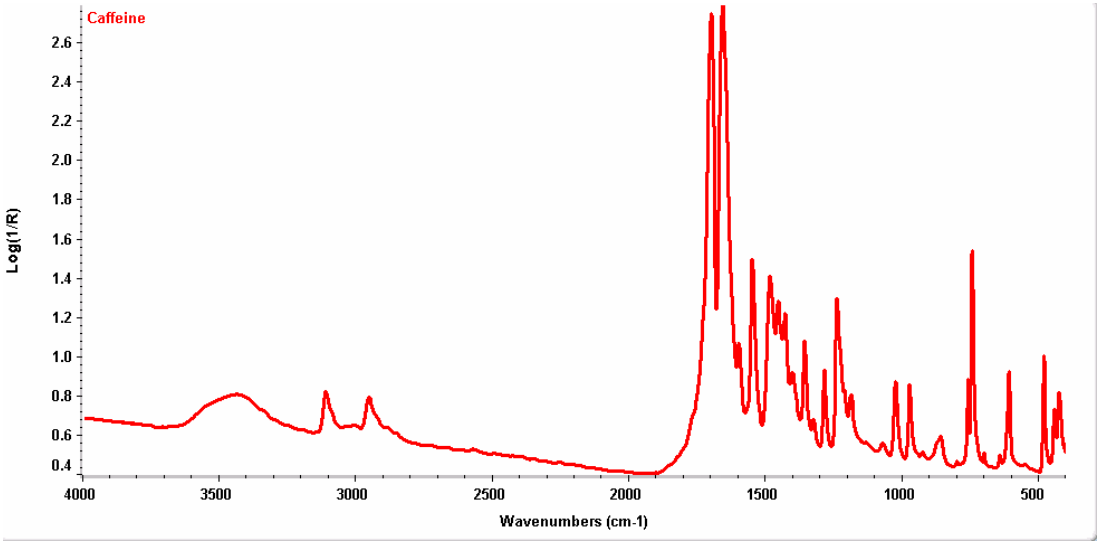


Kubelka - Munk Conversion

Process | Other Conversions….| Kubelka - Munk or, prior to sample analysis, select Kubelka - Munk under Final Format in Collect | Experiment Setup | Collect tab

An unconverted spectrum collected using diffuse reflectance compared to a converted spectrum. This should be done to compare data to transmission library data.

Experimental Results - Scatter



Common Problem with Diffuse
(try to correct by re-grinding sample)

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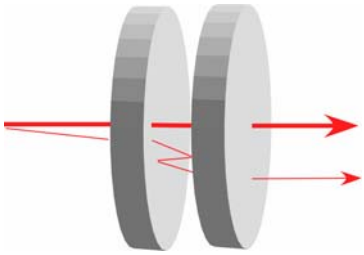
A common problem with diffuse reflection analysis is scatter. Any time you work with powered samples, or samples which may have a scratched surface this can occur. Recall that this is a frequency dependant loss of energy. As the wavelengths become shorter they are more effectively lost. This results in a uniform tilt in the absorbance (or –Log R) baseline.

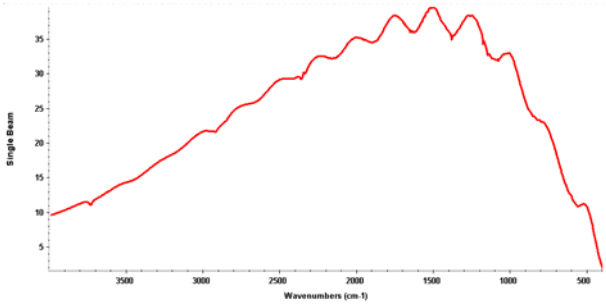
This should be corrected by preparing the sample again and re-grinding to smaller particle size.

If you can not prep the sample again, you could perform a baseline correction.

Fringing

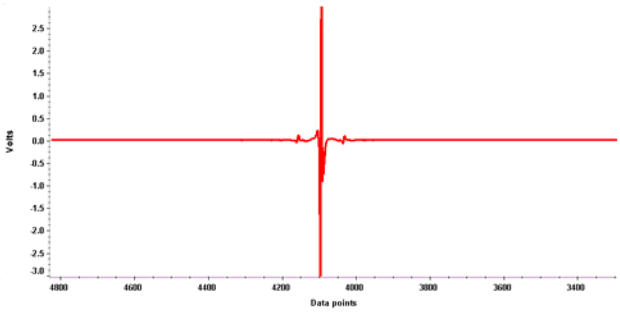


Secondary interferogram representing optical pathlength difference



Fringing Problems

Occurs when energy passes through two or more smooth, flat, parallel surfaces with different refractive indicies



Since the refractive index of the surfaces is greater than air we observe a sine wave function after the Fourier transformation

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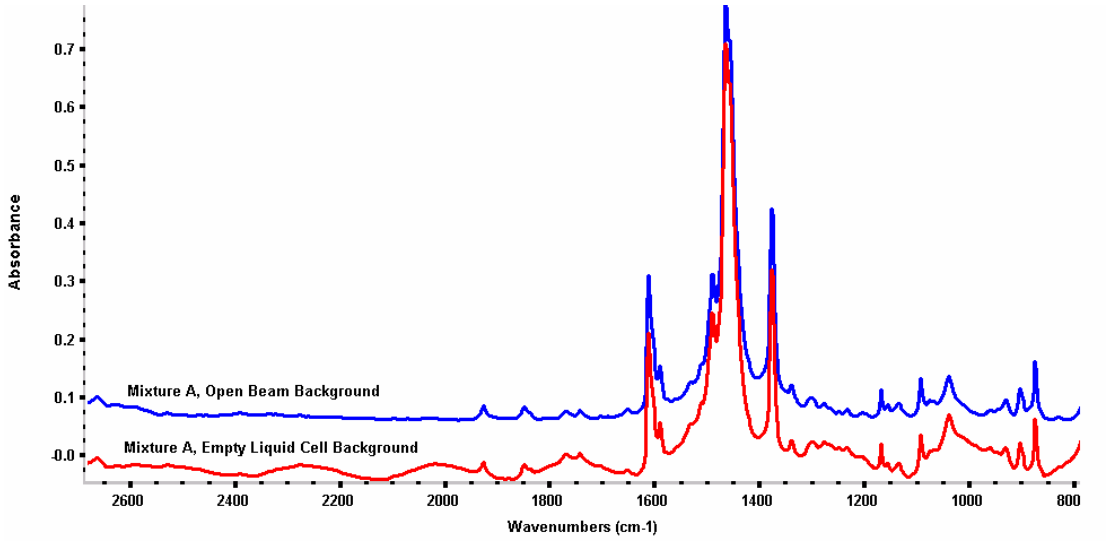
Fringing (sometimes called channeling) can occur when light is sent through 2 or more smooth, flat, parallel surfaces. Note that between each surface is a gap, usually filled with air. The refractive index (n) of the surfaces is greater than the refractive index of air.

As the infrared beam passes through the cell, some portion of the light will be reflected between the windows, causing it to travel an additional distance to reach the detector. This increase in optical path difference produces a latent interferogram, sitting next to the primary interferogram. When Fourier transformed, a cosine wave is generated in the single beam spectrum.

Note that this can occur with two or more surfaces, and can also occur in thin films that have parallel flat surfaces. The effect is common in either transmission or reflection measurements where this criteria is met. The sample becomes a fixed path interferometer and the different wavelengths in the spectrum will experience constructive/destructive interference producing the “fringing effect”.

Fringing



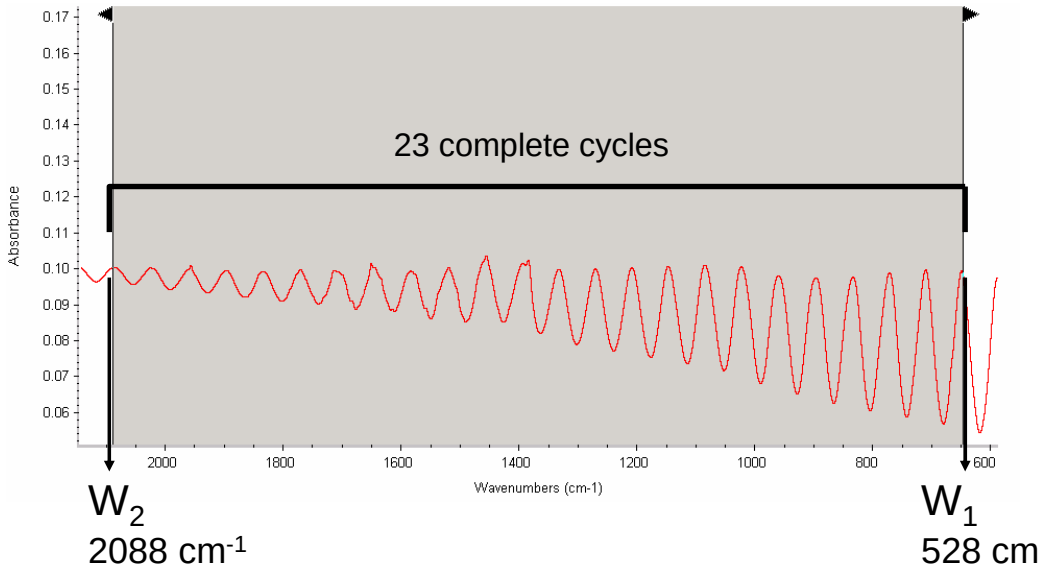
When a background containing a sine wave function (upper spectrum) is used to ratio against an empty sample cell (lower spectrum) we observe a cosine wave

When the single beam spectrum containing the sine wave is used as a background and ratioed against sample single beam spectrum the cosine wave now appears in the baseline of the spectrum. It is pervasive throughout the spectrum. It must be removed experimentally. There are currently no processing options available to remove this effect in OMNIC.

The top spectrum was collected using an open beam background -- nothing in the sample compartment. A better choice would have been to use a single IR window, made of the same material, that is twice as thick as the windows used for the liquid cell.

Remember why the fringing occurs: two or more, smooth, flat, parallel surfaces and a refractive index change. If one of those conditions can be altered, fringing will not occur or can be reduced to an acceptable level. Try to roughen the surface of the sample or holder (with polymer films, put on a matte finish) or tilt the sample, or remove one surface completely.

Calculating pathlength from interference fringes



Length (in cm) = # of complete cycles / 2 * (W_2 - W_1)

Length = 0.007 cm

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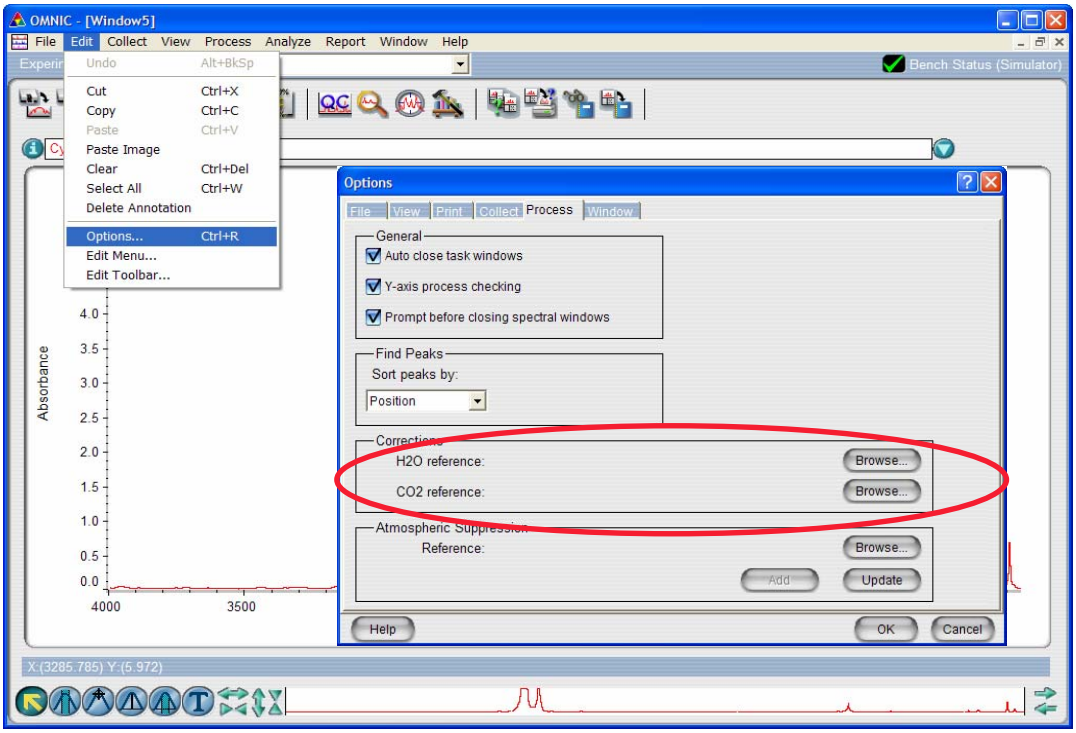
Remarkably, we can use fringing to our advantage. Fringes may be used to calculate the thickness of the gap between surfaces.

First collect a background with nothing in the sample compartment. Now, collect a "sample" of the empty liquid cell. This will produce a spectrum of containing just the cosine wave. With this in hand, count and record the number of complete cycles that occur across a fixed and known region. Use the formula above to calculate thickness. This simplified version of the formula is only valid when the infrared beam is passing through the sample with a normal angle of incidence.

Note: this is a simplified equation, where the refractive index is assumed to be 1.0 (air) and the angle the light is entering the sample is perpendicular to the surface (angle (θ) = 0 degrees). The more complete equation is:

Length (in cm) = # complete cycles / (2 * (W_2 – W_1) * (RI^2 – $Sin^2\ \theta$)$^{0.5}$)

Additional Processing - H_2O and CO_2 Correction



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Before water and carbon dioxide can be removed from a spectrum, a reference spectrum of atmospheric water and carbon dioxide in your facility must be acquired on your system and the location of the reference spectrum must be identified in the configuration.

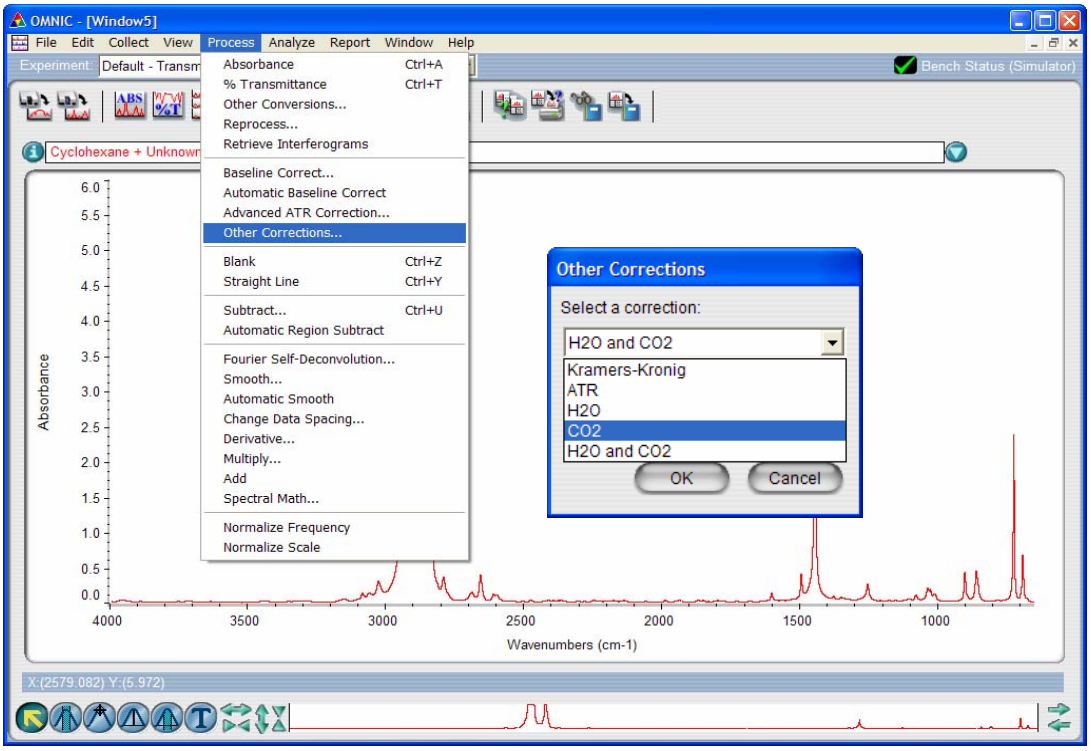
First you must collect a spectrum of water and carbon dioxide. This is accomplished by closing the sample compartment and allowing as much atmospheric contamination to purge as possible. If you don't have a purged system, close the sample compartment overnight. Collect a background first thing in the morning. Then, open the sample compartment and collect a sample. Be sure to set your spectral range from 4000 to 400 cm^{-1}.

Once collected, save the spectrum to your hard drive using a name you remember and note the location. Select Edit | Options | Process Tab. Using the Browse button find your newly collected water and carbon dioxide spectrum on the hard drive. If you intend to correct both water and carbon dioxide, do this for both water and carbon dioxide.

After locating the water and carbon dioxide reference you may want to save your configuration again to preserve this information

It is important that the reference spectrum be collected using the same optical configuration as you will be using for the samples. This may require that you have multiple reference files on the disk, one for each technique you will be correcting.

Additional Processing - H_2O and CO_2 Correction

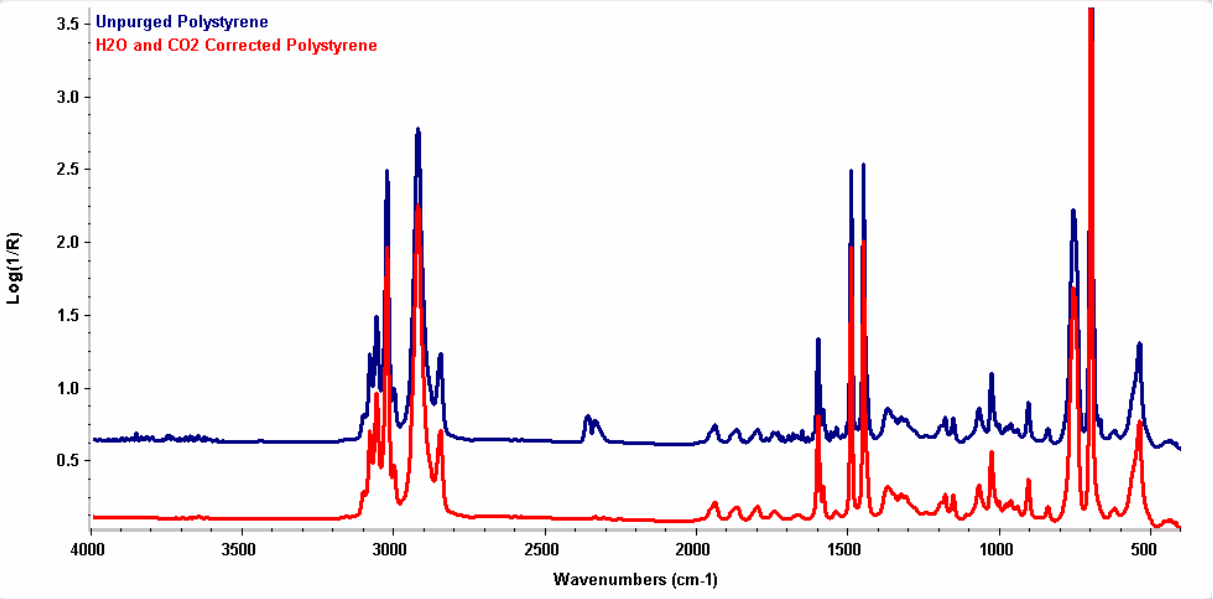


To perform the correction simply select Process | Other Corrections. You may then select from H_2O, CO_2 or both H_2O and CO_2.

When the correction is performed the software automatically measures the amount of water and carbon dioxide in your sample spectrum and subtracts. Because this is altering data, it is best suited to cosmetically improve the data or to enhance a library search. We don't recommend using this or any other corrections if you are doing quantitative analysis because it adds one more variable to your method.

It is advisable to replace your water and carbon dioxide reference spectrum periodically, especially if you are in a region where the humidity changes as the seasons change.

Additional Processing - H_2O and CO_2 Correction



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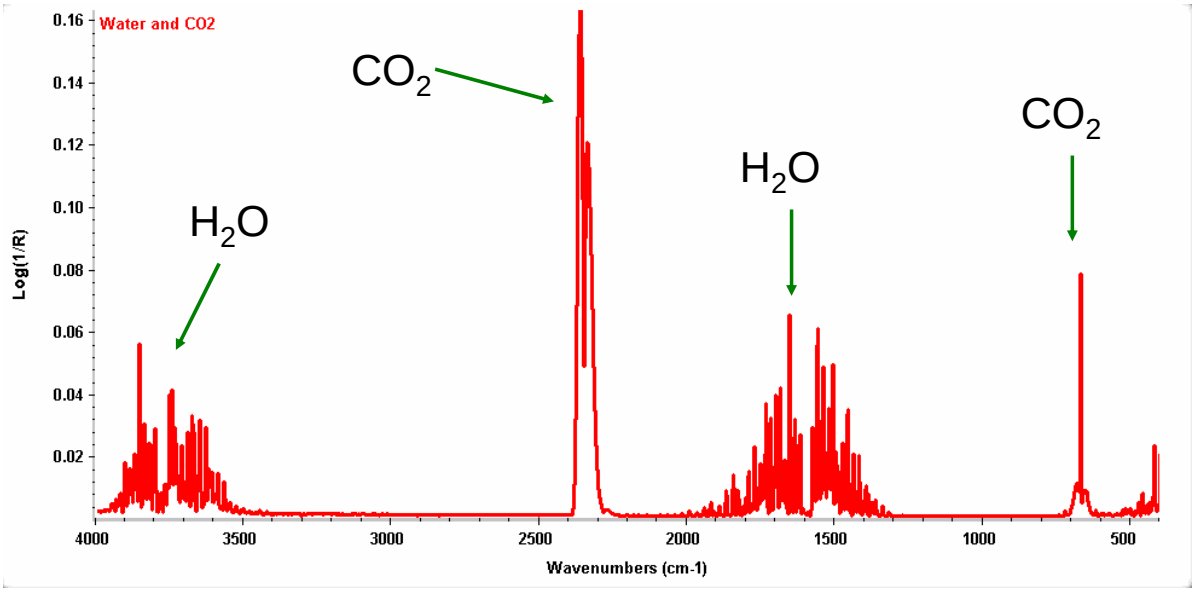
This is the result of water and carbon dioxide corrections.

Additional Processing - H_2O and CO_2 Correction



To Use H_2O Correction, collect reference data from 4000 to 1250 cm^{-1}

To Use CO_2 Correction, collect reference data from 4000 to 600 cm^{-1}

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A final note:

If you intend to correct for water then be sure to collect your reference spectrum from 4000 to at least 1250 cm^{-1}. If you intend to correct for carbon dioxide you must collect your reference spectrum from 4000 to at least 600 cm^{-1}. This is because the software needs these regions in the reference to accurately calculate the amount of contamination present in your samples. Keep this in mind when collecting your reference spectrum, especially if you have an accessory with a cut off.

You need not worry about these cutoffs for sample data. The software will simply ignore these regions in sample data.

The resolution of the reference spectrum must match the resolution of your sample data. You can collect a reference spectrum that will allow for variable resolution by saving the interferogram of the reference spectrum. This will allow the software to automatically reprocess the reference to the needed resolution that matches your sample data. Only resolutions equal to or less than the reference will be matched correctly.

H_2O and CO_2 Correction Summary

- Setup appropriate Spectral Range
- Collect Background with as little atmospheric H_2O and CO_2 as possible (well purged, keep cover closed and slightly vented)
- Collect Sample with sample compartment open
- Save Spectrum to Hard Drive
- Select Edit | Options | Process Tab

  -“Point” to H_2O and CO_2 spectrum using Browse Buttons

  - Select File | Save Configuration As for future use
- Select Process | Other Corrections | H_2O, CO_2 or H_2O and CO_2

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There are several steps to using water and carbon dioxide corrections. This summarizes the steps for quick reference.

Troubleshooting Spectral Results - Review

Specular

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Water Vapor and Carbon Dioxide Correction