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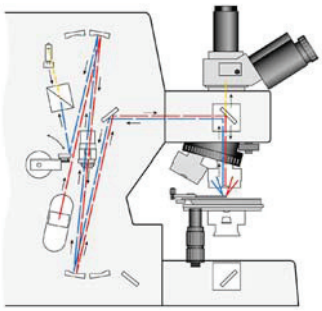
Reflection Analysis



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Objectives

Different Reflection Techniques

- *Reflection/Absorption*
- *Specular*
- *Diffuse*
- *Attenuated Total Reflectance*

Advantages and Disadvantages of Reflection

Sampling Challenges of Reflection

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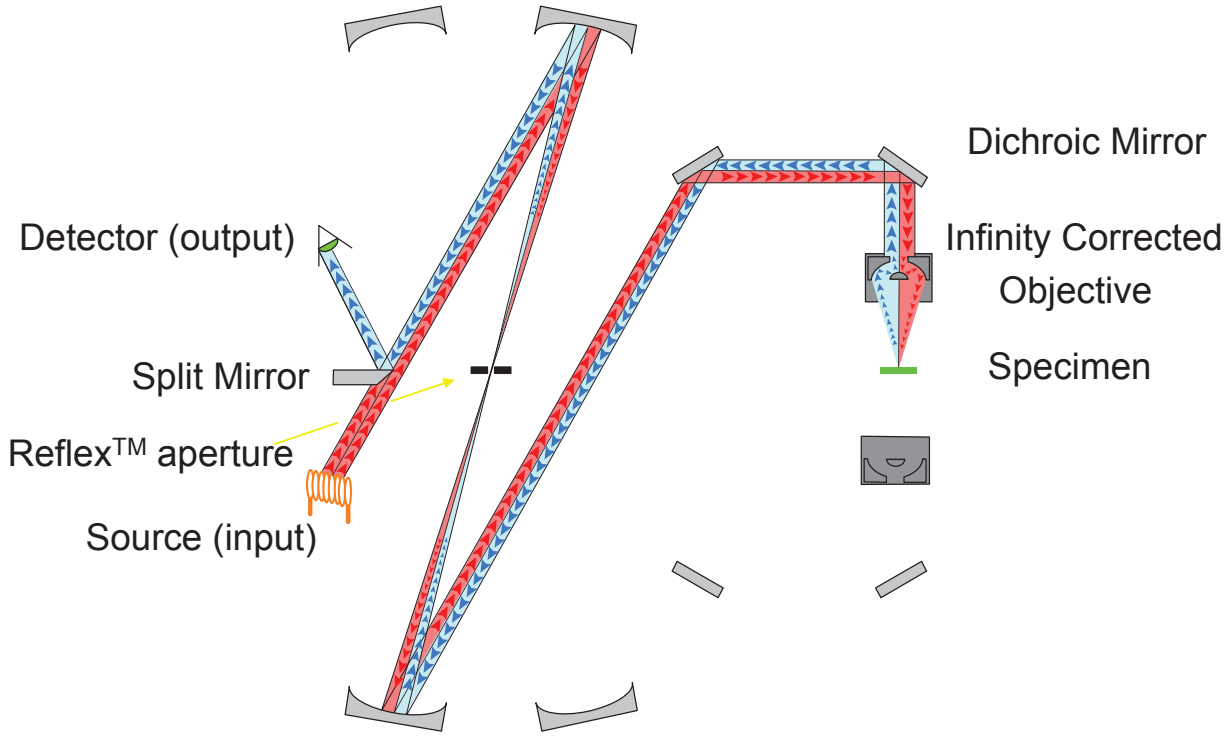
During this presentation, the following topics will be covered: The different reflection techniques, advantages and disadvantages of reflection, and the sampling challenges faced during reflection analysis.

IR Reflectance Path Diagram



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Reflection alignment is much easier than transmission alignment. The condenser should be safely stowed by bringing it to its lowest setting. Since energy will be transmitted and collected from the objective, the expected performance is worse than transmission performance. Note the split mirror used to direct the reflected energy to the detector. For transmission analysis this mirror is rotated out of the beam path.

Benefits of Reflection Analysis

- **Fast and Easy - Little sample preparation**
- **More versatile than transmission**
- **Non-destructive**
- **Provides very good quantitative data when using microscope**
- **Microscope configuration simpler for reflection - no condenser needed**

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A number of situations will arise in which transmission analysis is out of the question. Either the sample is very difficult to manipulate or the process requires a non-destructive analysis. In order for a material to provide good reflection information it needs to be flat and have good reflectivity or have a reflective material underneath it. As long as these conditions are met, reflection analysis can yield excellent results.

Disadvantages of Reflection

- **Surface analysis - does not provide information of the whole sample matrix**
- **Data collected needs to be manipulated for qualitative comparisons to transmission. Conversions not perfect**
- **Sample must have specific physical characteristics for optimal interactions**

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There are considerations for reflection techniques that may cause problems in the analysis of the data. Reflection is used primarily for the analysis of surface material. As such, any inconsistencies in the surface may cause the experiment to provide less than optimal information. The loss of light energy due to surface anomalies can shift the spectrum in many ways. Other types of samples may leach materials to the surface which can make the timing of an experiment critical.

Regardless of the type of reflection technique selected, the data acquired is different than the transmission equivalent. This in and of itself is not a problem. However, when trying to compare the reflection data to the transmission data for qualitative analysis the differences may be insurmountable. Corrections may be applied to improve the comparison but they do not completely eliminate the differences.

Reflection Techniques

- **Specular Reflection**
- **Reflection/Absorption**
- **Diffuse Reflection**
- **Attenuated Total Reflection**

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These are the four main categories of interactions which are measured using various reflection techniques. They are not the only options available but, collectively, they cover a very broad array of sampling types.

Reflection Analysis - Collecting the Background

- **The best background would create no spectrum but would have the same reflectivity as the sample (hard to find)**
- **Typically, a mirror is substituted (gold or aluminum)**
- **Shifts spectrum away from ideal**
- **An increase in the total background energy creates a shift in the spectral baseline**

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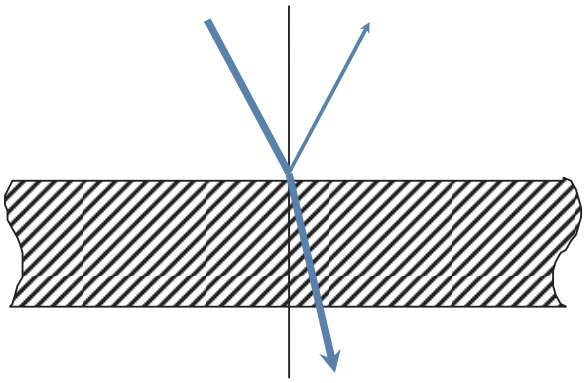
Unfortunately for this type of experiment there is no ideal background material. Therefore, a substitute must be chosen which allows for some degree of consistency or reproducibility. A clean mirror or piece of machined metal is sufficient.

Specular Reflectance



- Derivative shape peaks (result of frequency dependent dispersion of refractive index of sample) need to be corrected via Kramers-Kronig transform

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Specular reflectance occurs when light energy is reflected off the surface of the sample at an angle near normal. The reflected energy is then collected at the same angle. The interaction that occurs at the reflection point is what is being measured.

Specular Reflectance

- Surface technique
- Sampling depth approximately 5 μm
- Interaction from single reflection
- Smooth surfaces critical for reproducible collections (Quantitative Analysis)
- Good technique for mapping experiments
- Correction needs to be applied for qualitative analysis (Kramers-Kronig)

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If the conditions are right, specular can provide excellent results. Care must be taken to ensure that the sample is flat and smooth to achieve good results. Abnormalities in the sampling are difficult to compensate for mathematically.

Specular Reflection

- **The amount of light reflecting from the sample surface is affected by a number of factors**
  - **Surface structure (should be flat)**
  - **Angle of incidence (should be constant)**
  - **Sample refractive index**
- **The percentage of reflected light ranges from approximately 2% - 10%**
  - **Low throughput experiment**
  - **Increase number of scans to increase S/N**

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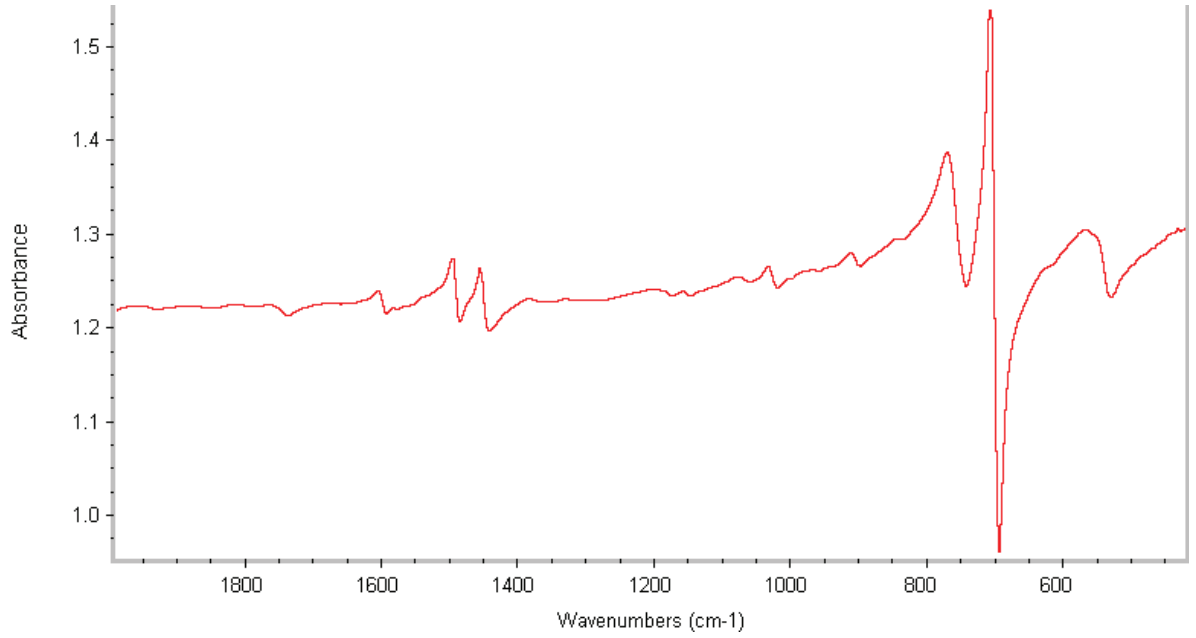
The amount of light that reflects depends on a number of different variables. The reflectivity of the sample changes continually across the frequency range of interest. The implication is that there will be more or less energy available for analysis depending on the frequency being measured. This fluctuation in energy throughput will cause changes to occur in the total energy being measured relative to a reference background.

Specular Reflectance Data



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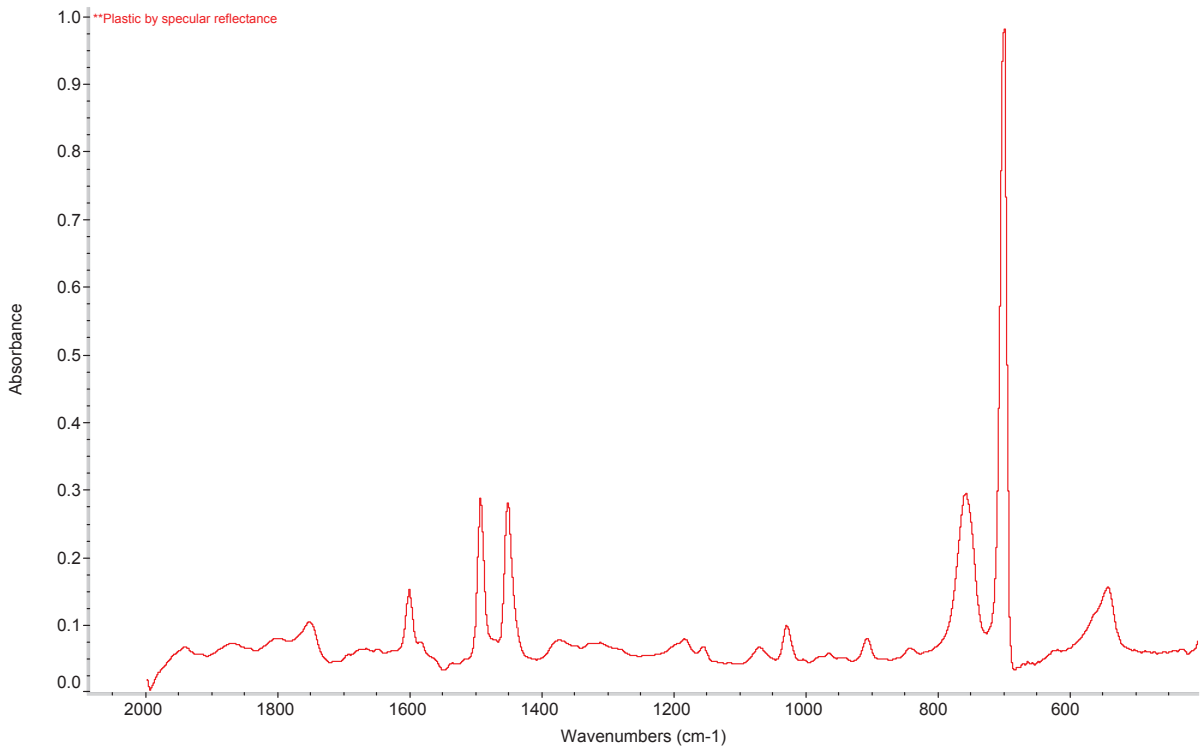
The combination of interactions combined with the shift in energy due to the non-ideal background causes the appearance of the acquired data to be non-conventional. Don't let the appearance fool you. This is perfectly good data. Quantitatively the goal is ease and reproducibility of which both are obtained. Any quantitative analysis should use this form of the data along with the PLS algorithm provided in the TQ Analyst software.

For accurate results when utilizing a search library there will need to be a correction made to this data.

Specular Data - Kramers-Kronig Corrected



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After the Kramer-Kronig correction, the specular data can be compared to transmission libraries.

This correction assumes some parameters and in doing so yields a best approximation to the transmission data set. Because of these assumptions, this correction rarely works across the entire mid infrared range. Target regions should be selected that will yield the most information from the spectrum when searched against a transmission library.

To Correct or Not to Correct?

- **Qualitative analysis**
  - Apply the Kramers-Kronig correction
  - Clean up the spectrum as much as possible
- **Quantitative analysis**
  - Do not apply any corrections
  - Check the sample/experiment for reproducibility

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Summary of Specular Reflectance

- Sample surface critical for good data
- Extremely simple experiment - Focus and collect
- Conflicting variables along with non-ideal background create bizarre spectra
- Best case scenario - Great quantitative and qualitative data
- Worst case - Total garbage!

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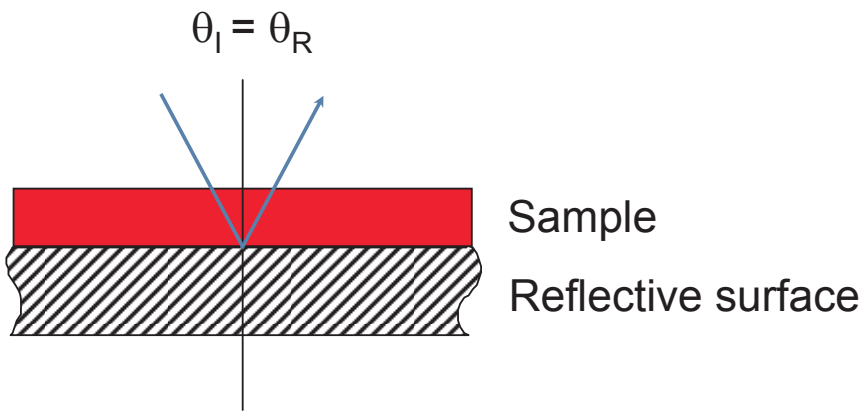
Reflection Absorption

- Angle of incidence of approximately 30°



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In this experiment the light passes through the coating material to the reflective surface and back out. In order for this experiment to provide clean data the surface of the coating as well as the surface of the underlying material need to be smooth. Any rough surface will scatter the infrared energy and will cause inconsistencies in the measurements.

Reflection Absorption

- **Technique which utilizes the same optical configuration as a Specular experiment**
- **Looking at thin films on reflective surfaces (thickness ranges approximately 1-50 μm)**
- **Used for contaminant analysis, coating thickness measurements, curing times, quality control, etc…**
- **Data generated is very clean**

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Even though it is classified as a reflection technique, the data generated is the result of a transmission interaction. This provides very clean data for both qualitative and quantitative analysis.

Sampling Considerations

- Two surfaces involved - The sample and the underlying, reflective material
- Internal reflections create an interference pattern
- Sample too thick or too thin for other techniques
- Particulates in the coating
- Multiple layers, soda can lining

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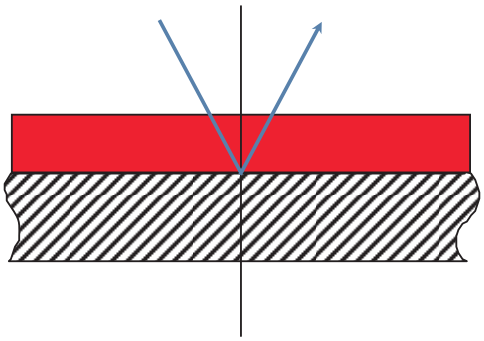
Sample/Background Collection

- **Focus on surface and collect sample**
- **If surface of sample is slightly irregular, collect multiple points to generate an average if performing quantitative analysis**
- **If scattering occurs, correct the baseline before qualifying sample and applying Kramers-Kronig, if needed**
- **Sample provides a natural background be cleaning off top layer to reveal underlying reflective surface**



Multiple reflection points can cause sinusoidal wave

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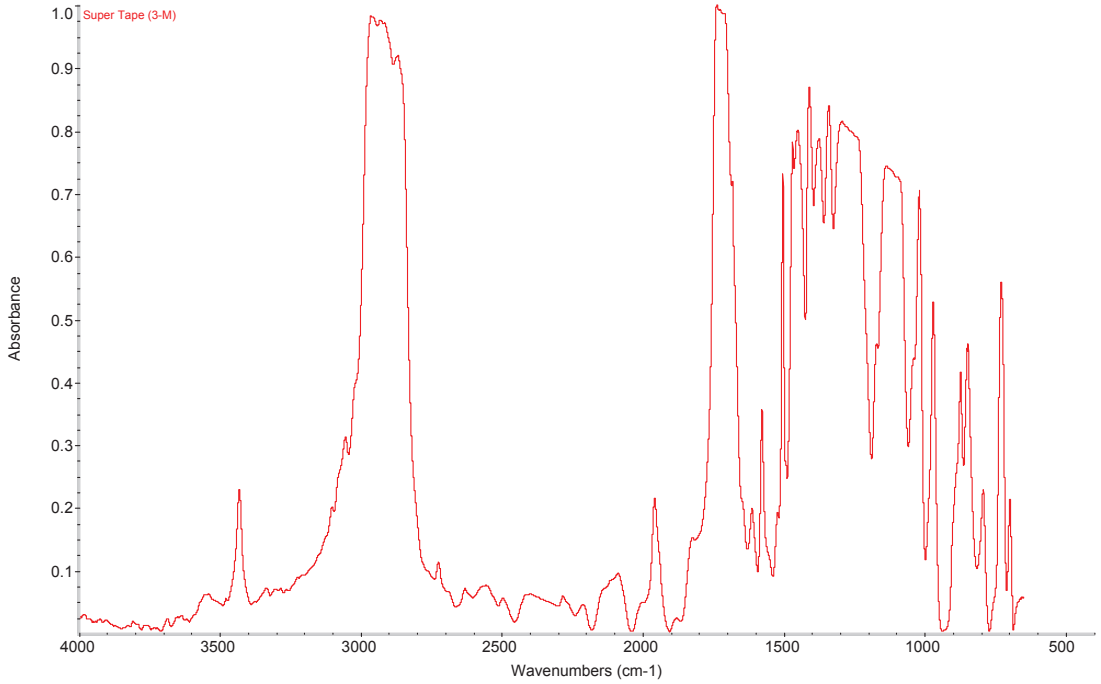
Tape Sample by Reflection Absorption



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Here a reflection absorption spectrum is nearly identical to a transmission spectrum. In many ways, this type of analysis can be thought of as a double transmission analysis because the infrared energy will pass through the sample twice. This often leads to totally absorbing bands if the sample is too thick so care must be taken in preparing the sample for analysis.

Grazing Angle Objective

Submicron thickness films on metals

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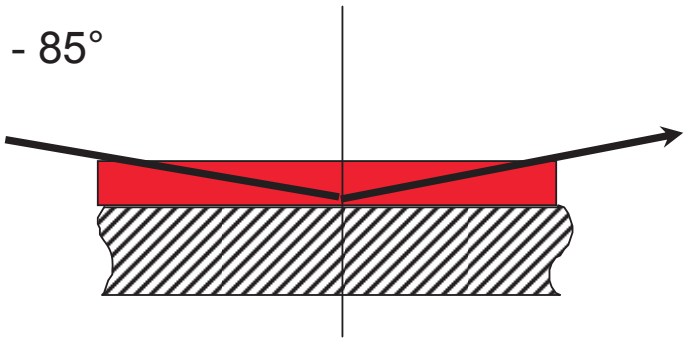
The grazing angle objective has a specific optical path defined by an aperture that only allows the more extreme angles to pass through to the sample surface. This creates a low energy situation. The loss of energy will be manifested in the sensitivity of the experiment. It is not uncommon for the number of scans required to clean up the noise to run into the thousands.

Advantages of Grazing Angle

- **Angle of incidence greatly increased**
- **5X increase in pathlength over 32X objective**
- **Range of coating thickness - 20 Angstroms to 1µm**

$\theta_1 = 65 - 85°$



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In reflectance spectroscopy, very thin films pose a unique problem to the IR spectroscopist. As we have learned, when using reflection absorption spectroscopy, incident radiation passes through the sample at a given angle and reflects off the substrate at a complementary angle before passing through the sample again and being collected at the detector. The pathlength is greater than the transmission pathlength due to this double pass. But what about very thin films 1 μm to as little as 10 Å, where there isn't enough pathlength to get any data? If the sample is on a metal reflective surface, the use of a Grazing Angle objective may be the solution.

Monolayers Analysis by Grazing Angle Reflectance Spectroscopy

- **What are the uses of Grazing Angle Reflectance Spectroscopy?**
  - **Analyze very thin films including molecular monolayers**
  - **Determine thickness of monolayer films**
  - **Perform molecular orientation studies on monolayer films**

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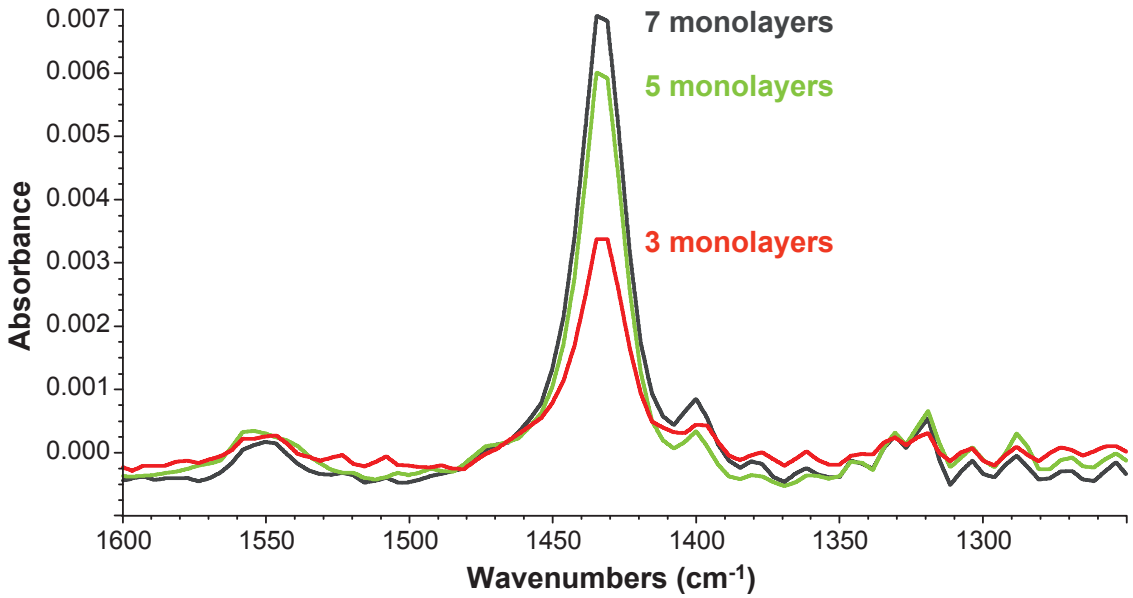
Grazing angle measurements are commonly used to measure ultra-thin films from 1 μm to 10 Å. Even monolayer films can be analyzed with grazing angle when they are on reflective metal surfaces. Grazing angle analysis can be used to measure thickness and study molecular orientation.

Cadmium Arachidate Monolayer 80° Angle of incidence



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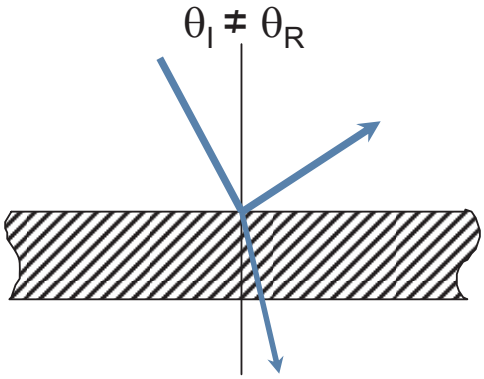
These are spectra of samples of Cadmium Arachidate monolayers on a gold substrate. Data is shown for samples with 3, 5, and 7 monolayers deposited.

Diffuse Reflectance



Near normal angle of incidence.
The Angle of incidence does not equal angle of reflection

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Diffuse reflectance is typically utilized as an analysis method for powders or granular samples. Using this method, some energy scatters off of the sample surface at angles other than the incident angle.

What Makes it Work?

- **Some energy scatters off of the sample surface at angles other than the incident angle but all information is collected**
- **Most energy absorbed into the sample surface**
- **Silicon Carbide tips allow scraping of sample surfaces**
- **Kubelka-Monk conversion helps to relate to transmission data**

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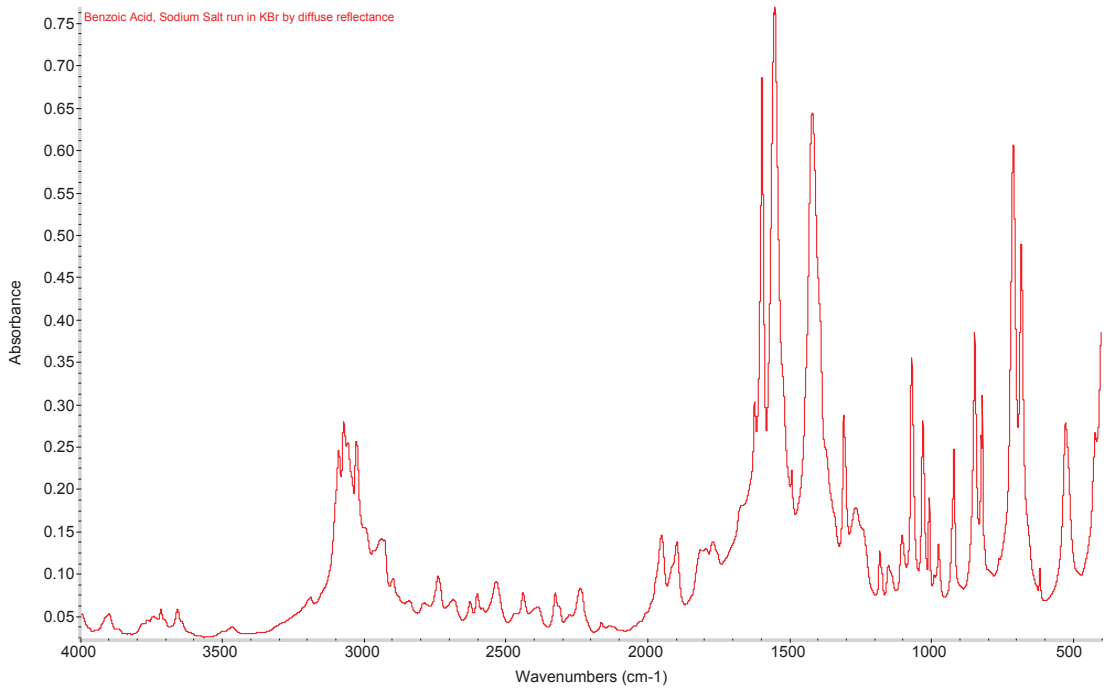
The energy from the incident beam hits the surface and a small percentage reflects. The reflected light contains the absorbance information from the structure of the sample surface.

Benzoic Acid by Diffuse Reflectance



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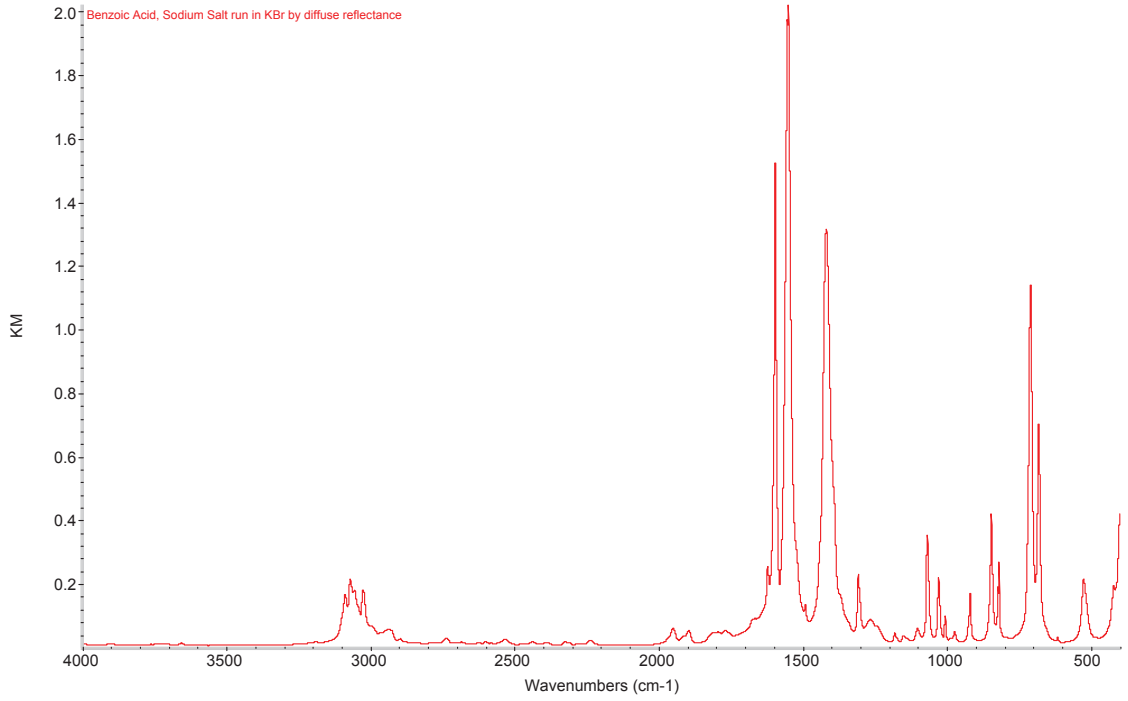
This is a spectrum of Benzoic Acid in KBr taken by diffuse reflectance. In many cases, the concentration of samples analyzed using the diffuse reflection technique do not vary linearly with log (1/R) (which is the equivalent of absorbance for reflection measurements) this is due to pathlength variation. The Kubelka-Munk scale was developed to provide a more linear relationship with respect to concentration.

Kubelka-Munk Conversion Applied



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Select Kubelka-Munk in the Other Conversions dialog box to convert %reflectance spectra collected using the diffuse reflection (DR) technique to Kubelka-Munk units. These units are similar to absorbance units. As a result, the Kubelka-Munk format is useful for visually comparing diffuse reflectance spectra against absorbance spectra in commercially available libraries.

Because this is a CONVERSION and not a CORRECTION, no effect will be seen in the search results.

Reflection Microscopy Conclusions

- Usually faster and easier than transmission
- More susceptible to sample structures
- Information provide will need corrections to be used with transmission data
- Quantitatively, no corrections needed
- Background collection can be difficult

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Summary

Different Reflection Techniques

- ***Reflection/Absorption***
- ***Specular***
- ***Diffuse***
- ***Attenuated Total Reflectance***

Benefits and Disadvantages of Reflection

Sampling Challenges of Reflection

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During this presentation, we have learned: the different reflection techniques, advantages and disadvantages of reflection, and the sampling challenges faced during reflection analysis.