Remembering main principles of FTIR
- ATR & its applications to materials
- IRRAS and applications to materials
- A bit about FTIR Microscopy
- Summary
When does an absorption occur?

- The frequency of the light matches the frequency of the vibration (resonance)
- The dipole of the molecule must change
- The dipole must change in the same direction as the electric field vector
  - Important for oriented films or some polymer matrices
What do we mean, “Dipole Change?”

- Stretch HCl, the dipole (charge separation) increases.
- \( \text{N}_2 \) has no dipole and can’t be made to have one by vibrating.

Molecular Vibrations

- Stretching
- Deformation
Polyatomic Molecules

- The spectrum becomes more complex as the number of bonds increases

![Graph showing wavenumbers and fingerprint region for polyatomic molecules.](image)

The Michelson Interferometer, heart of IR instrument

- Fixed mirror
- Beamsplitter
- IR Source
- Detector
- Varying path difference

![Diagram of the Michelson Interferometer with labeled components.](image)
Fast Fourier Transformation

Interferogram $\xrightarrow{\text{FFT}}$ Spectrum

Transmission Spectrum

Interferograms $\xrightarrow{\text{Single Beams}}$ Ratio $\xrightarrow{\text{Spectrum}}$
The Three Major Optical Components

The Detector
- Detects the IR light

The Beamsplitter
- Splits light into two, interfering beams

The Source
- Emissions IR light

Put them together and you get…

The FTIR Spectrometer
Choose components to set spectral range

<table>
<thead>
<tr>
<th>SPECTRAL RANGE CONFIGURATIONS</th>
<th>Visible</th>
<th>Near-IR</th>
<th>Mid-IR</th>
<th>Far-IR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duro-Varian (2500-2500 cm⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duro-Varian (1500-2500 cm⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beam splitters</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz (14,000-1,200 cm⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KBr (9000, 7000, 5000 cm⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detectors</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inorganics and polymer modes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Overtones; Glass containers
- Raw material id
- Fundamentals; Salt windows or ATR; Structure or identity
- Low energy; Salt windows; Inorganics and polymer modes

FT-IR Sampling Techniques

Improve Your Measurements with the Appropriate Sampling Tool
Sampling methods

- Transmission
  - Excellent for solids, liquids and gases.
  - The reference method for quantitative analysis
  - Sample preparation can be difficult

- Reflectance
  - Collect light reflected from an interface
    - Air/sample, solid/sample, liquid/sample
  - Analyze liquids, solids, gels or coatings
  - Minimal sample preparation
  - Convenient for qualitative analysis, frequently used for quantitative

Transmission Analysis

- Technique for many reference methods
- Solids, liquids, gases
- Qualitative analysis
- Quantitative analysis
- Maximum sensitivity
- Low cost
- Proper pathlength required
  - Complicates sample prep and setup
### FT-IR Reflection measurements

- **Attenuated total reflectance (ATR)**
  - The infrared beam reflects from an interface via total internal reflectance
  - The sample must be in optical contact with the crystal
  - The collected information is from the surface

- **Diffuse reflectance (DRIFTs)**
  - Solids and powders, diluted in a IR transparent matrix
  - The information provided is from the bulk matrix

- **Specular (external) reflectance**
  - Sample must be reflective or on a reflective surface
  - The information provided is from the bulk

### Attenuated Total Reflectance (ATR)

- Versatile and non-destructive technique for infrared sampling
- Requires minimal or no sample preparation
- Useful for surface characterization

![Smart ARK ATR](image1)

![Smart Orbit Diamond ATR](image2)

![Smart Performer ATR](image3)
Attenuated Total Reflectance (ATR)

**Single Bounce** vs. **Multi-bounce**

- Small sampling area
- Use for strong absorbers
- Solid samples
- Broad sampling area provides greater contact with the sample
- Use for weak absorbers or dilute solutions

Considerations for ATR Analysis

\[ d_p = \frac{\lambda}{2\pi n_{atr} \left[ (\sin^2 \theta) - \left( \frac{n_{sample}}{n_{atr}} \right)^2 \right]^{1/2}} \]

- Refractive index, angle of incidence
  - Pathlength!
- Spectral range of interest
  - Transparency of crystal
- Phase of sample: solid, liquid, gel
- Chemical properties of sample (acid, base)
- Hardness of sample
Properties of ATR Crystals

Chart of Common Crystal Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>ATR Spectral Range (cm⁻¹)</th>
<th>Refractive Index</th>
<th>Depth of Penetration (µ) (at 45° &amp; 1000 cm⁻¹)</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germanium</td>
<td>5.500 - 675</td>
<td>4</td>
<td>0.66</td>
<td>Good for most samples. Strong absorbing samples, such as dark polymers.</td>
</tr>
<tr>
<td>Silicon</td>
<td>8.900 - 1.500 &amp; 360-120</td>
<td>3.4</td>
<td>0.85</td>
<td>Resistant to basic solutions.</td>
</tr>
<tr>
<td>AMTIR</td>
<td>11,000 - 725</td>
<td>2.5</td>
<td>1.77</td>
<td>Very resistant to acidic solutions.</td>
</tr>
<tr>
<td>ZnSe</td>
<td>15,000 - 650</td>
<td>2.4</td>
<td>2.01</td>
<td>General use.</td>
</tr>
<tr>
<td>Diamond</td>
<td>25,000 - 100</td>
<td>2.4</td>
<td>2.01</td>
<td>Good for most samples. Extremely caustic or hard samples.</td>
</tr>
</tbody>
</table>

ATR in the analysis of materials

- Bulk Polymers like pellets, chunks, pieces
- Polymer films
- Multi-layer Polymer films
  - Bi layer
  - Multi-layer, by varying angle of incidence of beam and using spectral subtraction.
- Liquids, gels and pastes

*Application notes available on subject of ATR analysis*
Analysis of Door Seals: Diamond Vs. Ge

- Need versatility: Diamond is excellent for most materials; Ge excels for HCB rubbers

Specular Reflectance

- Measure reflectance directly from a surface
  - Typically a specular (mirror-like) reflectance
  - $\theta_{\text{incidence}} = \theta_{\text{reflection}}$
- Incident angle influences…
  - effective pathlength
  - polarized IR response
- Polarization dependent effects
  - Use of polarized light improves s/n and can tune results for specific structural information
Reflectance / Absorbance Spectroscopy

- A "reflection", but spectrum dominated by "Absorbance" information
- Nicknames:
  - IRRAS
  - RAIRS
- Ideal setup - film on metallic surfaces
  - Au, Ag, Al, steel, etc.
- Thick films produce a folded-path transmission spectrum

Thick film R/A spectra

- Film on Aluminum
  - The "soda-can" experiment
- Note –
  - Reflection from film surface may alter spectra
  - Choose accessories to minimize effects

Thin film R/A studies on metals

- External reflectance is flexible in experimental arrangements
  - Reaction Chambers & other apparatus
    - Electrochemical
    - Liquid
  - Large specimens

Polarization modulation approach to IRRAS

- Polarization Modulation IRRAS
  - The polarization is modulated
  - Produces differential absorbance
  - Polarization independent species eliminated from spectrum, e.g. water vapor, or other gases in experiment.
- Monolayer studies

Source: Prof. J. Boerio, Univ of Cincinnati
PM-IRRAS Applications

- Poly-l-lysine on Au
  - Regular grazing angle
  - 80°, 400 scans
  - No purge
- Poly-l-lysine on Au
  - PM-IRRAS
  - 83°, 100 scans
  - No purge

SAM’s on gold

Wavenumbers (cm⁻¹)

Benefits of IRRAS

- Simple examination of thin and thick films
- Non-destructive, Non-contact
- Detailed structural information available
- Adaptable to many experimental arrangements
**TGA-FTIR, Another Powerful tool!**

- **TGA** measures weight loss over time with increasing temperature for polymers and other materials.
  - Determines residual volatiles, additives, decomposition & combustion products of sample.

- **Drawback:**
  Very little is known about the nature of the materials evolving from the TGA

- **FTIR** can be powerful extension to TGA
  - Gases are analysed by FTIR as they evolve out of the TGA instrument.
  - Spectra are collected over time and can be searched against libraries of gaseous materials to be better identified

- Combination of both techniques makes for much better understanding of initial sample.

*Detailed application note available upon request*
Monitoring specific components from TGA-IR

Conclusions - Sampling Techniques

- Infrared sampling techniques are the interface between the sample and the spectrometer – adaptable to many research applications
- Spectrometer systems can be configured to fit the speed, resolution, and sensitivity needs of your experiments
- Let us know how we can help solve your analytical problems!
FTIR Microscopy

Another powerful tool

Viewing the Sample

- IR and visible beam paths collinear
  - Superior sample image
  - Improved IR throughput
- Infinity corrected optics (Nicolet™ Continuum™ microscope)
  - Optional viewing technology
- Adjustable focal length infrared objectives
- Binocular Viewer
Infrared microscopy sampling chart

Sample can be removed from its bulk / media

1 - TRANSMISSION
- Flatten (rolled) sample
- Salt window (NaCl)
- Measure the sample in TRANSMISSION: Collect background thru the salt window by using same aperture size. When Reflachromat condenser is available, compensate for window material (typically 2.0 mm) both objective and condenser.

2 - TRANSMISSION
- Compressed sample
- Salt windows (NaCl) or diamond
- Measure the sample in TRANSMISSION: Collect background thru the cell by using same aperture size. When Reflachromat optics are available, compensate for window material (typically 2.0 mm) both objective and condenser.

3 – RAS reflectance analysis
- Flat the sample onto an EZ Spot Au or Al coated glass slide by using the roller knife.
- Collect background onto a clean area of the reflective substrate.

Sample can't be removed from its bulk / media

4 - REFLECTANCE
- Thick, infrared opaque sample
- Sample holder
- Measure the sample in REFLECTION: Collect background onto a gold / reflective surface by using same aperture size. If the sample is a thin layer on a back reflecting surface it will be a RAS analysis. If it is thick or opaque, Reflectance measurement will occur.

5 - Micro ATR
- ATR crystal
- Measure the sample in micro ATR: Collect background thru the crystal.
Reflachromat™ optics – Multilayer sample

- Transmission mode
  - No compensation (left)
  - Compensated (right)

Sample
Salt windows

Reflachromat™ provides the best transmitted visible image obtainable from IR-Vis Objectives and Condensers

Polymer laminate cross-section
Sampling with IR microscope (mapping)

- **Discrete points**
  - The stage moves to each specified location
  - Only spectra from those locations are collected

- **Line maps**
  - The stage moves along a line dragged across the sample
  - Number of spectra depends on line length and step size

- **Area maps -> 2D images**
  - The stage moves until a complete area of the sample is completed
  - Spectra within the whole area are collected

Aerospace Technology

- CCD Device used in space exploration failed
- Contamination is not visible with standard illumination or polarization
- Identify contamination & source of problem

15X Reflachromat Objective
Transmission DIC Illumination
ATR, Si Crystal

Spectrum of contaminant

Spectrum of Poly(propylene glycol)

Polymer Laminate by Transmission

Polymer Laminate Cross Section

PET

EVA

PE

Cellulose
Line Map of Polymer Laminate

- Automated characterization of polymer laminate
- Sample prep - roller knife
- Mount in compression cell - NaCl windows
- Linear map, 2 micron steps
- Contiguous set of points collected across width of laminate
- Fully automated data collection

Contour Display of Polymer Laminate
Waterfall Display of Laminate Spectra (Chemical Profile)

Spectra from Polymer Laminate

Adhesive Layer

Polymer Laminate Line Map: Point 10 - Polyamide

Polymer Laminate Line Map: Point 35

Polymer Laminate Line Map: Point 29 - Polyethylene
Summary, FTIR Microscopy

- Powerful tool to characterize very small samples
- Lots of valuable information available
- Many applications to materials analysis
Most of all…

- **THANK YOU FOR YOUR TIME AND ATTENTION!!**

- **All the best for 2007**

- For more information:
  Mathieu Gosselin
  514-369-2276
  mathieu.gosselin@thermofisher.com