CENTRAL EXPERIMENTAL MULTIUSUÁRIO

UFABC

Descrição das técnicas e acessórios de medida do sistema de espectroscopia de absorção no infravermelho FT-IR 660 da Varian

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FUNDAMENTOS DE ESPECTROSCOPIA VIBRACIONAL

A espectroscopia vibracional envolve técnicas de espectroscopia capazes de sondar os estados vibracionais de uma amostra. As principais técnicas envolvidas são as espectroscopias Raman e de Absorção no Infravermelho (IR). Ambas são técnicas complementares e fornecem informações sobre a composição molecular, estrutural e interações moleculares em uma amostra. Em ambos os métodos os estados de energia vibracionais são excitados por luz. Nos ateremos aqui a técnica de IR.

Na IR, luz infravermelha de uma fonte contínua (usualmente 2.5 – 25 μm ou 4000 – 400 cm^{-1}) é diretamente absorvida de modo a excitar as moléculas para estados vibracionais mais altos. Do ponto de vista eletromagnético, a interação entre a luz e o material se dá via acoplamento entre o campo elétrico da onda luminosa e o momento de dipolo elétrico líquido presente nos átomos ou íons envolvidos na vibração molecular. A vibração modula o momento de dipolo presente. Em freqüências luminosas idênticas as das vibrações há maior absorção de energia o que se traduz em picos ou bandas no espectro de absorção da amostra. A técnica de medição mais sofisticada atualmente envolve o uso de um interferômetro de Michelson e a posterior transformada de Fourier do interferograma, a chamada Absorção no Infravermelho por Transformada de Fourier (FTIR).

Uma das grandes vantagens desta técnica é permitir analises não-destrutivas de substancias sólidas, liquidas e também gasosas.

Vários tipos de vibrações moleculares caracterizando diferentes moléculas podem ser encontradas no espectro IR. Elas podem ser simplesmente agrupadas em estiramento vibracional, deformações vibracionais e torções ou estruturas vibracionais. (vide Figura 1)

O movimento molecular envolvido depende da extensão de ligação e mudanças do ângulo de ligação, os quais movem individualmente átomos ou grupos de átomos levemente para fora de posição. Este evento de complexa movimentação dos átomos de moléculas envolve multiplicidade de energias, especialmente se os átomos possuem diferentes massas e estão conectados com diferentes tipos de ligações, tais como, ligações únicas, duplas ou triplas. Certas bandas observadas na região espectral podem definir classes de substâncias presentes na amostra [Kuzmany, 2009].

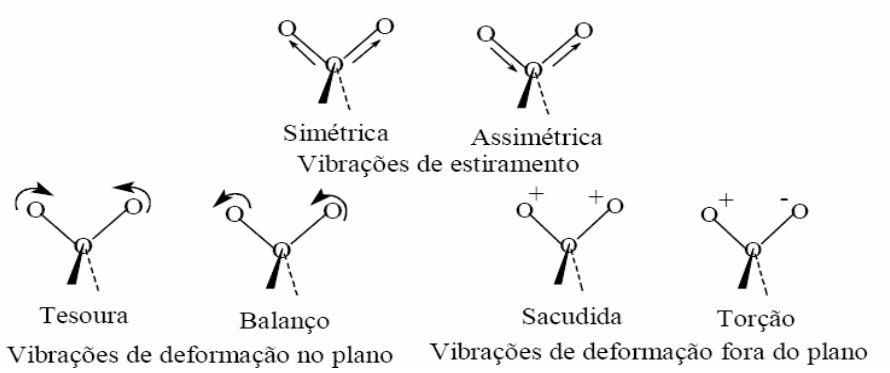

Figura 1 – Vibrações de um grupo de átomos (+ e – significam vibrações perpendiculares ao plano do papel) [Kuzmany, 2009].

O espectrômetro FT-IR 660 da marca Varian Inc. (Fig. 2) instalado na Central Experimental Multi-usuário da Universidade Federal do ABC (UFABC) tem como principais acessórios o sistema de micro-espectroscopia (microespectrômetro FT-IR 610 com micro-ATR - cristal de Ge), refletância especular (Pike 30Spec), e ATR (Pike MIRacle com cristal de ZnSe). Além deste, há uma prensa manual para confecção de pastilhas de KBr e uma célula para experimentos com óleos.

Figura 2. Sistema de microespectroscopia FT-IR 610/660 (Varian Inc.)

Espectroscopia por Transmissão

A coleta de espectros por transmissão no infravermelho é o método mais popular e o mais fácil de implementar visto que dispensa o emprego de acessórios mais complexos. Basicamente a amostra é instalada (vide Fig. 3) sobre o caminho óptico do feixe infravermelho sobre um porta-amostra adequado, que em geral é uma janela de material transparente ao infravermelho (CaF_2 ou KBr). Amostras sólidas necessitam ser diluídas em KBr em pó (1-5% em massa).

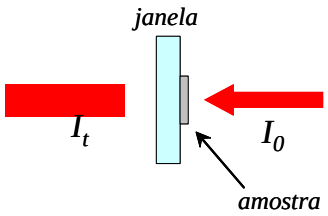

Figura 3. Esquema experimento FTIR por transmissão.

O espectro é apresentando em termos da transmitância ou absorbância da amostra, que varia em energias próximas a algum estado vibracional ou eletrônico da amostra. A transmitância, tendo em vista a configuração apresentada na Fig. 3, pode ser escrita como

$$T = \frac{I_t}{I_0} = e^{-\alpha lc}$$

onde α é a absortividade do material, *l* o caminho óptico e *c* a concentração. A absorbância é definida como

$$A = -\ln(\frac{I_t}{I_0}) = -\alpha lc$$

A Fig. 4 apresenta típicos espectros de transmissão e absorção no infravermelho. A região espectral que fornece informações relevantes encontra-se entre 500 e 4000 cm^{-1}. Estão também indicadas as regiões espectrais aonde as principais vibrações moleculares ativas no IR aparecem. Esta técnica tem fortes limitações quando se trata de amostras espessas ou ainda amostras fortemente hidratadas, requerendo complexo preparo prévio (diluição em KBr, confecção de pastilhas, secagens múltiplas, etc).

A opção de emprego da micro-espectroscopia por transmissão, o que pode auxiliar na diminuição da influência destes artefatos. Uma possibilidade a ser testada envolve a aplicação de um filme de amostra sobre uma janela de CaF_2 submetida à secagem a vácuo.

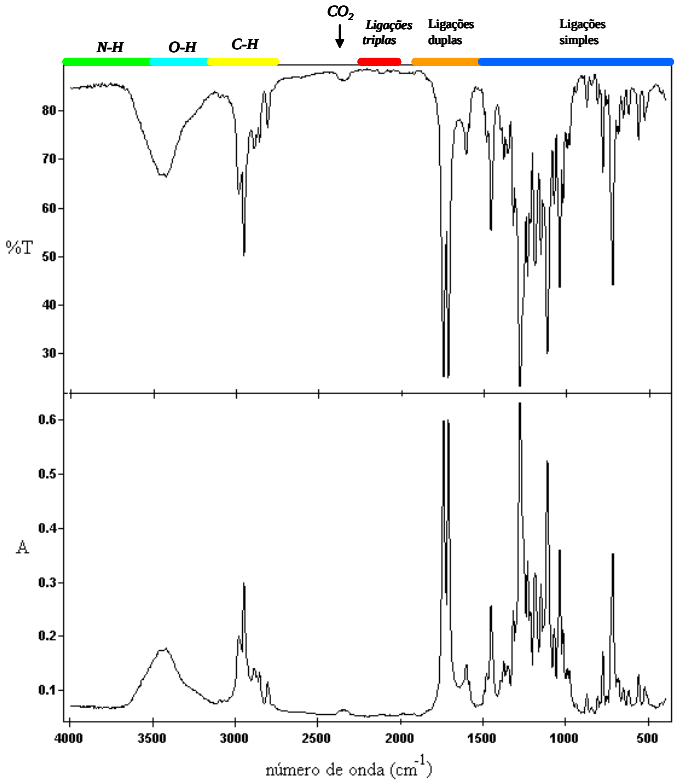

Figura 4. Típicos espectros de transmissão (painel superior) e absorção (painel inferior) no infravermelho. Estão também indicadas as regiões de vibração das principais ligações moleculares que podem ser identificadas por IR.

4.2.3 Espectroscopia por Refletância Especular

A técnica de refletância especular é bastante utilizada para medidas de filmes finos em substratos refletivos, análise de materiais "bulk" e medidas de camadas monomoleculares em substratos. Em geral é uma técnica que dispensa prévio preparo das amostras. Em essência a técnica fundamenta-se na medida da intensidade da luz infravermelha refletida pela superfície da amostra em determinado ângulo. O fenômeno eletromagnético envolvido depende basicamente do valor do ângulo de incidência, do índice de refração do material, da espessura do material e da polarização da luz incidente. Considerando a situação representada na Fig. 4, a intensidade refletida é dada por (Hecht, 2002)

$$I_r^s = I_0 \frac{\left[\frac{2r}{(1-r^2)}\right]^2 sen^2\left(\delta/2\right)}{1+\left[\frac{2r}{(1-r^2)}\right]^2 sen^2\left(\delta/2\right)}$$

com $\delta = \frac{4\pi}{\lambda_0} n_{amostra} d \cos\theta_t$ sendo a diferença de fase, d a espessura da amostra e r o coeficiente de reflexão da película de amostra. Esta última é dada pelas equações de Fresnel. Devido a dependência com o índice de refração, I_r^s irá variar muito em energias próximas aos níveis vibracionais por conta da chamada dispersão anômala. Assim, o espectro de refletância possuirá basicamente as mesmas informações vibracionais do que o espectro de transmissão.

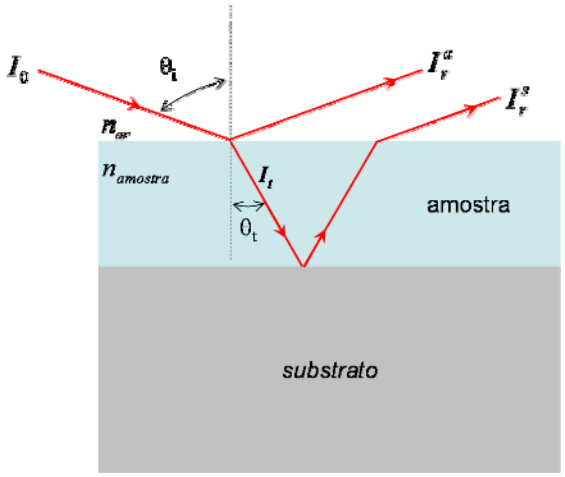

Figura 4. Caminho óptico de um feixe de luz incidente sobre uma amostra depositada em um substrato.

No caso de amostras suficientemente espessas ou fortemente absorvedoras, I_t será muito atenuado e a luz espalhada será essencialmente devido à reflexão especular direta, I_0.

O processo de reflexão seguirá essencialmente as equações de Fresnel. Neste caso, como ilustrado no Fig.6, a refletância aumenta consideravelmente para altos valores de θ_i e ainda dependerá fortemente do índice de refração do material. Isso pode trazer complicações experimentais sérias devido ao aparecimento de artefatos e distorções por conta de rugosidades na superfície que espalham difusamente a luz e não homogeneidade do índice de refração na amostra. Assim, a padronização do método de deposição do filme de amostra, a espessura correta do material a ser empregado são parâmetros chave para a obtenção de espectros adequados, reprodutíveis e livres de artefatos.

No acessório a ser utilizado a luz incide na amostra fazendo um ângulo $\theta_i = 30°$. O caminho óptico está indicado na Figura 5. As amostras podem ser alíquotas a serem depositadas numa lamina recoberta de ouro ou ainda material sólido em pastilha. O volume adequado de material será uma das variáveis a ser encontrada no trabalho, bem como o tempo necessário para a secagem do material (caso necessário).

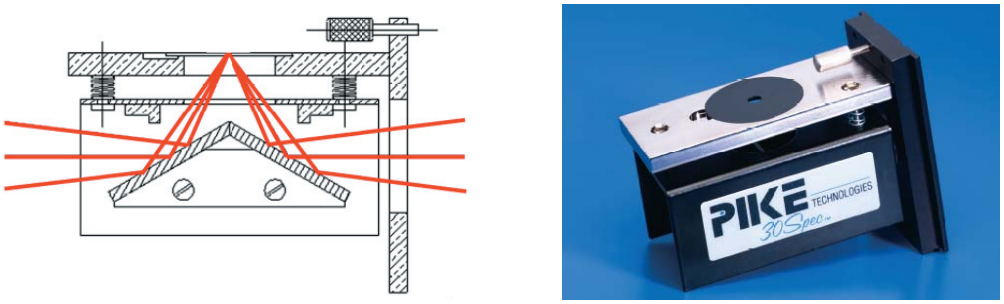

Figura 5. Painel esquerdo: traçado dos raios luminosos no interior do acessório de refletância especular 30Spec. Painel direito: Acessório de refletância especular.

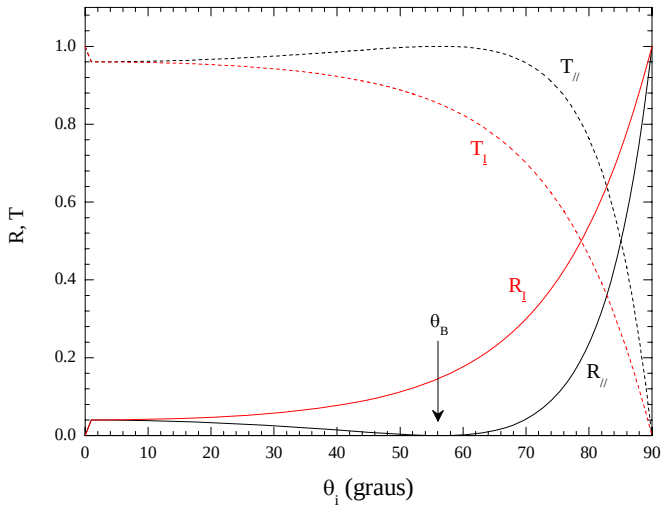

Figura 6. Refletividade e Transmissividade para material com índice de refração 1,50 como função do ângulo de incidência.

4.2.4 Espectroscopia por reflexão total atenuada (ATR)

Outra técnica muito empregada para coleta de espectros no IR é a refletância via reflexão total atenuada (ATR). Ela consiste basicamente em fazer incidir a luz sobre determinado um cristal transparente no infravermelho com ângulo de incidência maior do que ângulo crítico do cristal (θ_c). Este ângulo é definido como $\theta_c = \sin^{-1}\left(\frac{n_{cristal}}{n_{ar}}\right)$, onde *n* é o índice de refração. Nesta condição, $\theta_i > \theta_c$, ocorre o fenômeno de reflexão total, e não há, a princípio, luz transmitida. De fato, as condições de contorno na interface só podem ser satisfeitas caso haja algum campo elétrico propagando-se além da fronteira do material. A chamada onda evanescente, cuja intensidade decai muito rapidamente com a distância (Fig. 7).

Tipicamente o comprimento de penetração é da ordem de 0,5 – 2μm e depende basicamente do comprimento de onda da luz, do índice de refração do cristal e do ângulo de incidência

$$d_p = \frac{\lambda}{2\pi\left(n_{cristal}^2 sen^2\theta_i - n_{ar}\right)^{1/2}}$$

Ao posicionar uma amostra nesta região teremos a interação desta onda com a amostra e conseqüente absorção de luz IR. Esta configuração de experimento possui a vantagem de praticamente eliminar a necessidade de preparo prévio da amostra, sendo compatível com grande variedade de tipos de amostras. Outra vantagem relaciona-se a fina camada de material que é submetida à amostragem, o que possibilita minimização do sinal de interferentes, como a água, no espectro IR.

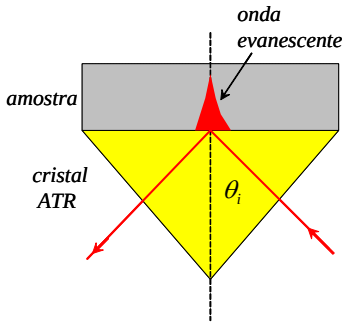

Figura 7. Esquema aparato de ATR.

Os acessórios de micro-ATR e ATR Pike Miraclen (Fig. 8) utilizam cristais de Ge e ZnSe, respectivamente. Em ambos os casos o ângulo de incidência é 45º e os comprimentos de penetração são 0.66 μm (Ge) e 2.00 μm (ZnSe). Uma das importantes variáveis a ser testada neste projeto é qual o cristal mais adequado ás condições experimentais impostas.

O acessório macro ATR Pike Miracle emprega um espelho de transferência diretamente ao feixe de infravermelho para um transmissor de infravermelho de cristal ATR. Um segundo espelho direciona o feixe emitido a partir da outra extremidade da chapa MIRacle para o detector confeccionado no espectrômetro FT-IR (Figura 9). A amostra é colocada sobre o cristal para a obtenção dos espectros FT-IR.

Figura 8. Acessórios de micro-ATR (à esquerda) e Pile Miracle ATR (à direita)

Figura 9. Esquema óptico do acessório de ATR Pike MIRacle.

REFERÊNCIAS

KUZMANY, Hans, Solid-state Spectroscopy: An Introduction, Springer Verlag, 2009.

HECHT, Eugene.. Optics. 4th ed.. Reading, Mass: Addison-Wesley, 2002.

Spectroscopic Creativity

Modern FTIR Sampling Tecniques

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FTIR Sampling Techniques – the most popular

- Traditional transmission sampling
- Attenuated total reflectance (ATR)
- Diffuse reflectance
- Specular reflectance

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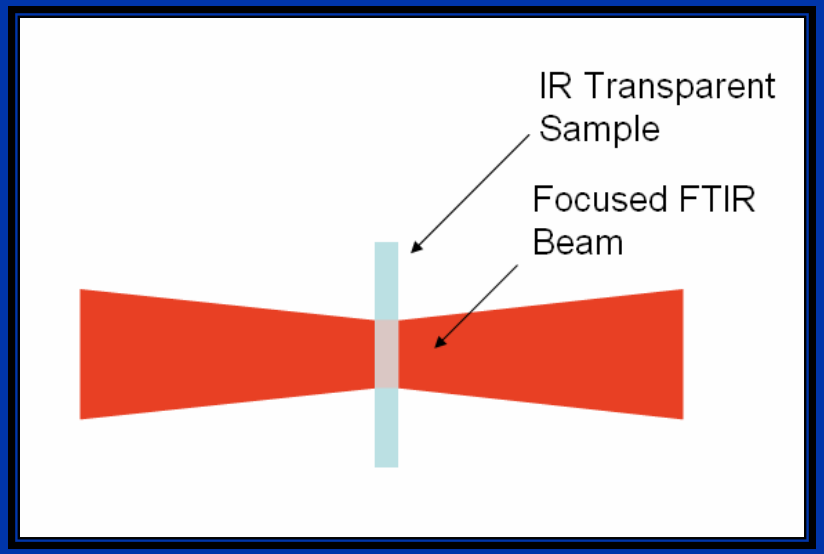
FTIR Sampling by Transmission



- Generally Highest Quality Spectral Data
- Consistent with Most Spectral Data Bases
- Qualitative and Quantitative Measurements
- Relatively Easy to Automate

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Spectroscopic Creativity

Basic Transmission Principles

$A = a \times b \times c$ Beer's Law

Where:
A = absorbance
a = absorptivity (sample dependent)
b = path length
c = component concentration

Sample Types: Solids, liquids, gases

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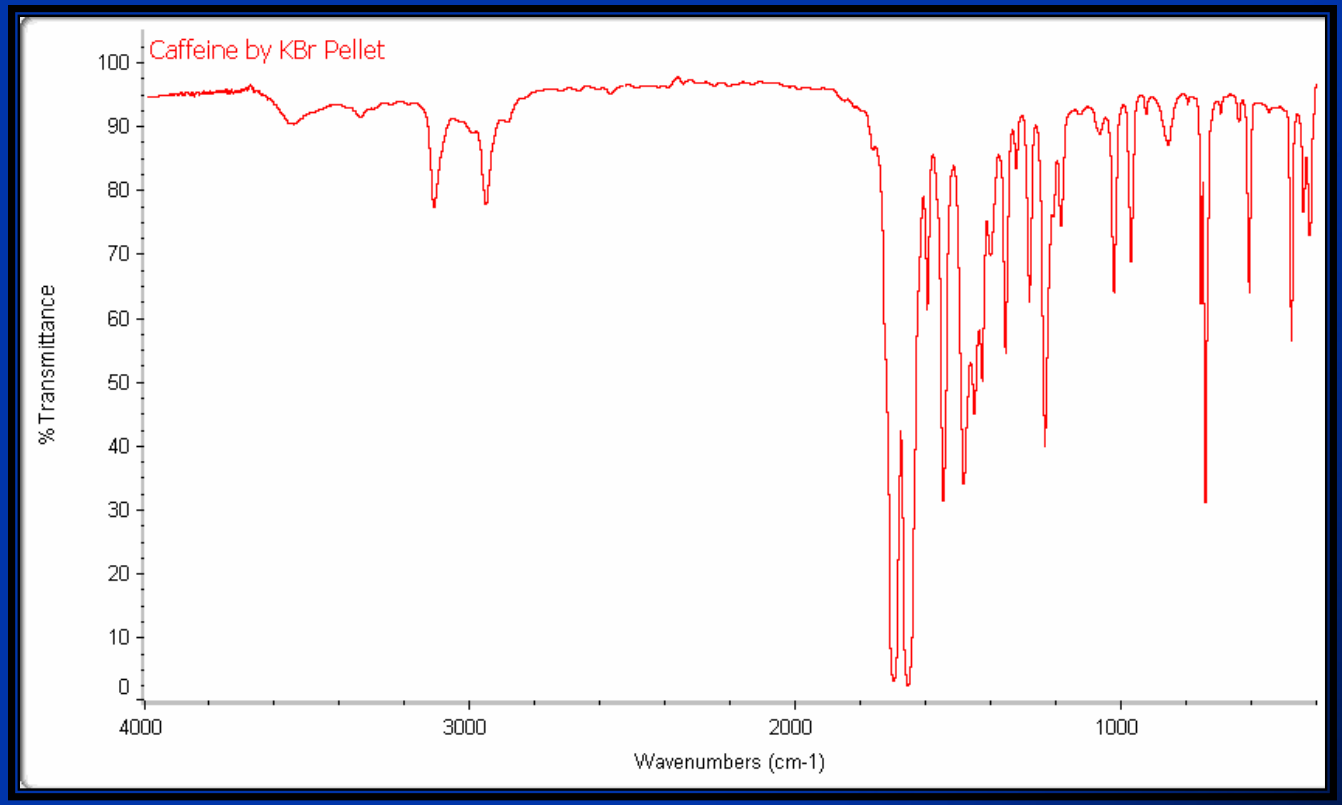
Spectroscopic Creativity

Transmission Sampling – Solid Samples



5 mg of Caffeine mixed with 100 mg of KBr in Wig-L-Bug and pressed into 13 mm pellet using the PIKE Evacuable Pellet Press and held in position using PIKE Sampling Card

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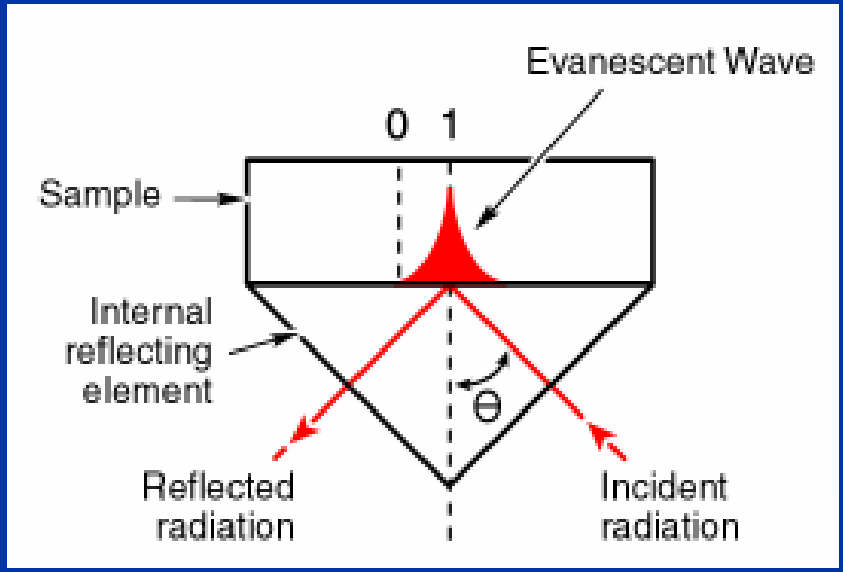
Benefits of FT-IR Sampling by ATR



- Generally Eliminates Sample Preparation
- Compatible with Most Sample Types
- Qualitative and Quantitative Measurements
- Fast and Easy to Use

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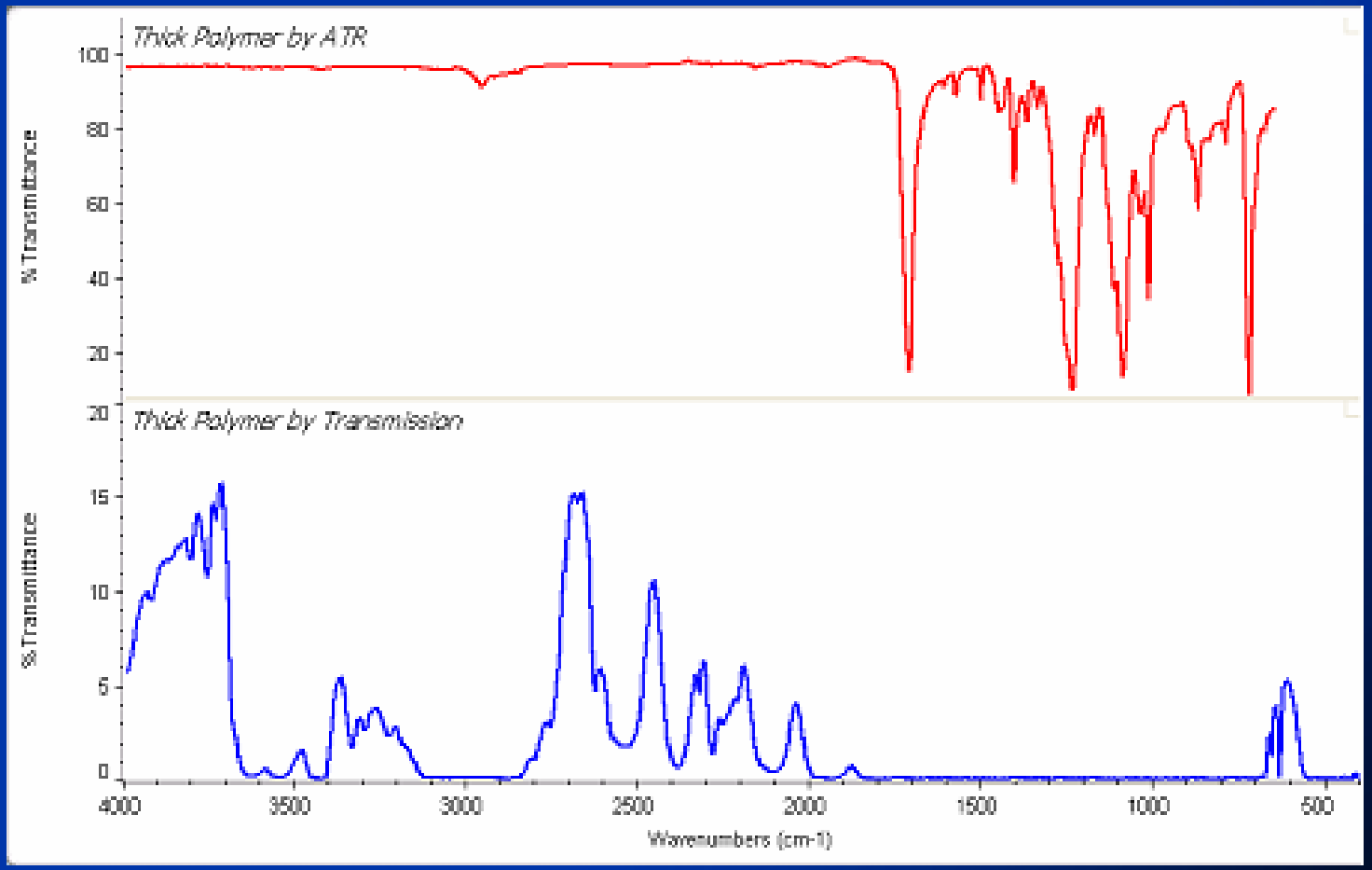
Spectroscopic Creativity

ATR Vs Transmission Sampling



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ATR Depth of Penetration – *probing the sample*

$$d_p = \frac{\lambda}{2\pi(n_1^2 \sin^2\theta - n_2^2)^{1/2}}$$

- Defined as the depth where E falls to e^{-1} of its value at the crystal surface
- For a given sample, probing depth is controlled by choice of n_1 and angle of incidence (θ)
- Wavelength dependence
- ATR accessory with variable angle of incidence and ATR crystal choice will provide depth profiling capability

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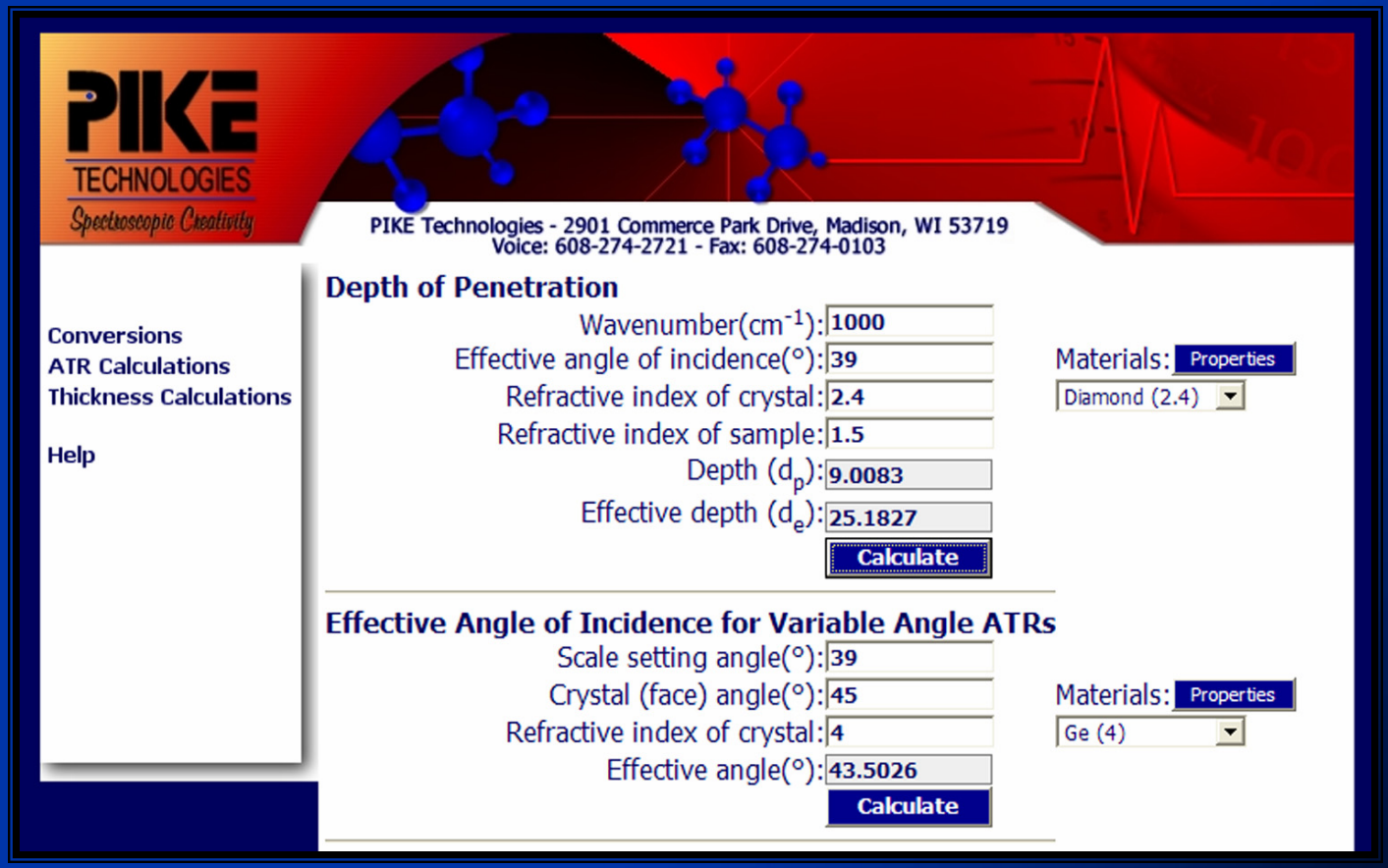
Spectroscopic Creativity

Calculate ATR Sampling Parameters



- Idea for ATR calculations

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ATR Products

- MIRacle – Single Reflection, Sample Identification
- GladiATR – Single Reflection Monolithic Diamond, Extreme Pressure, High Temperature
- HATR – Multi-Reflection, Highest Sensitivity for minor components
- ATRMax – Variable Angle, Multi-Reflection
- VeeMAX ATR – Variable Angle, Single-Reflection, Depth Profiling
- VATR – Classic Vertical Variable Angle ATR

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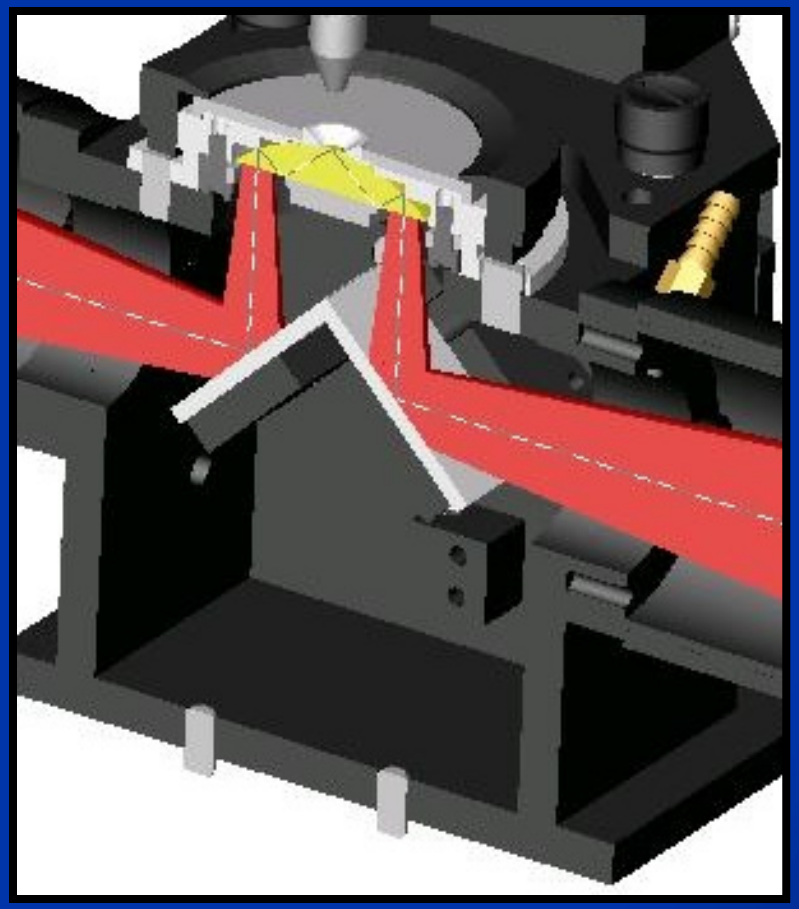
Spectroscopic Creativity

MIRacle ATR Technology



- Patented Optical Design
- Crystal Focuses IR Beam and Provides ATR Interface
- Highest IR Throughput
- Highest Spectral Quality
- Maximum Sampling Flexibility

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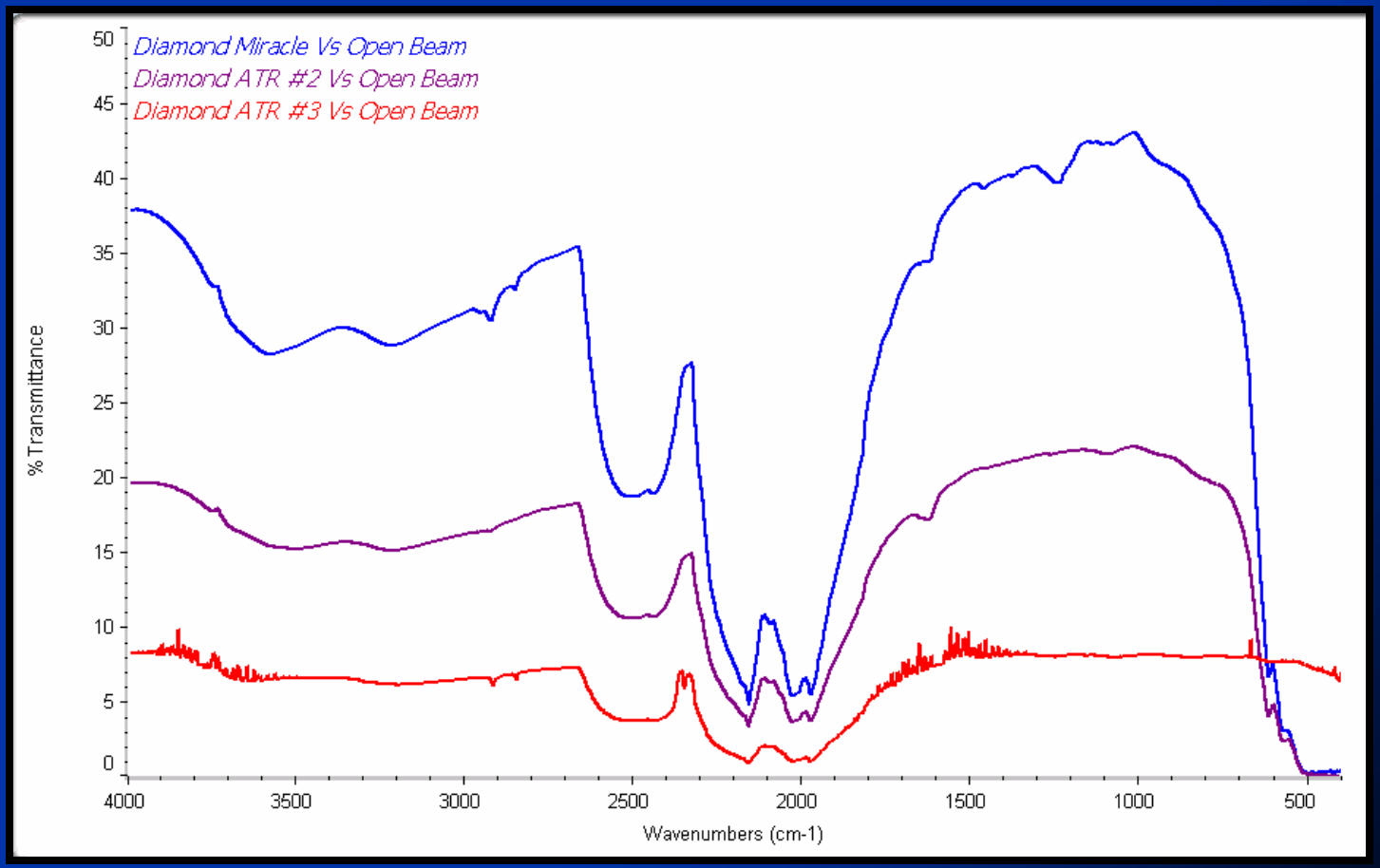
ATR Throughput Comparison



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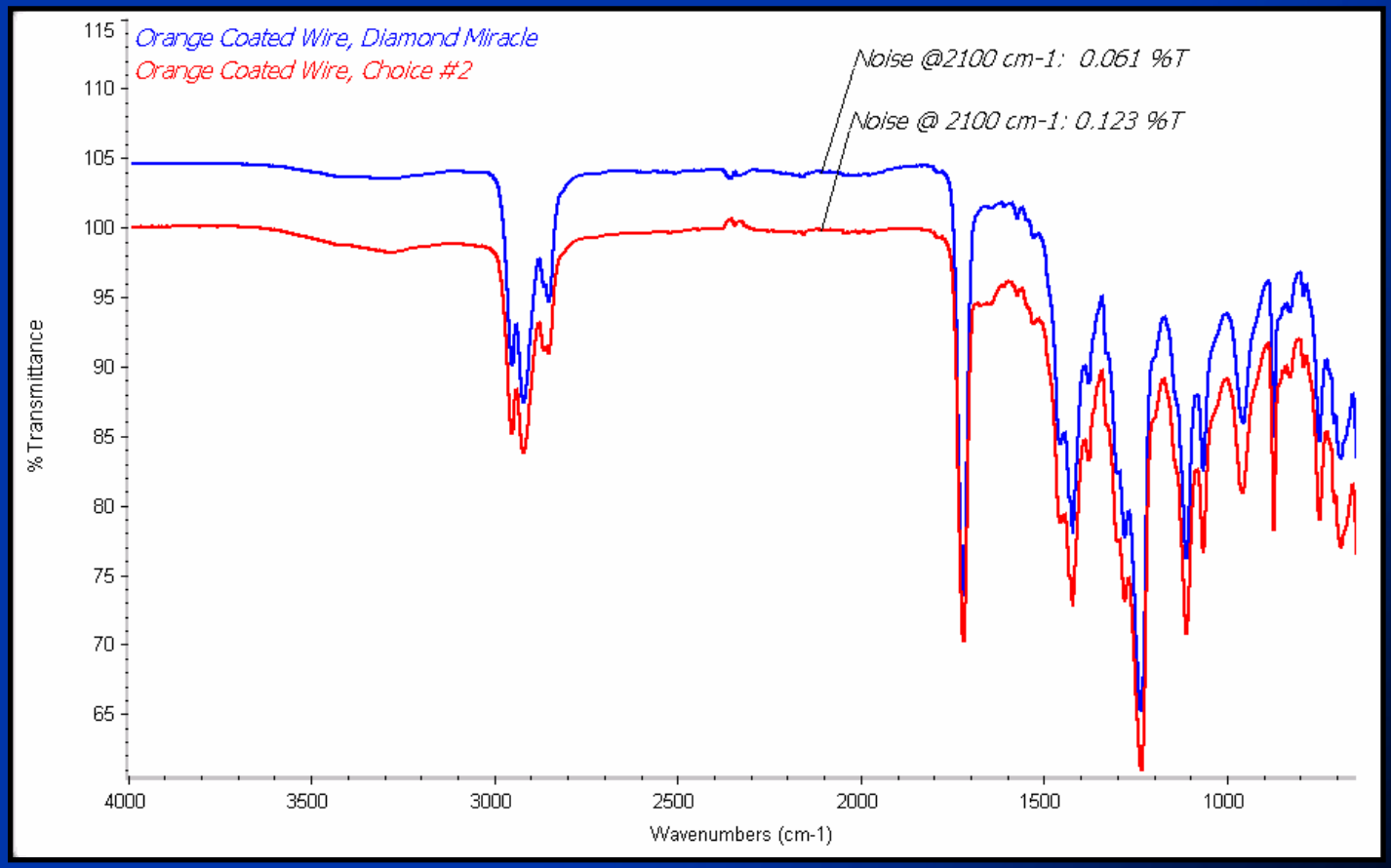
Higher Throughput = Higher SNR for ATR Spectra



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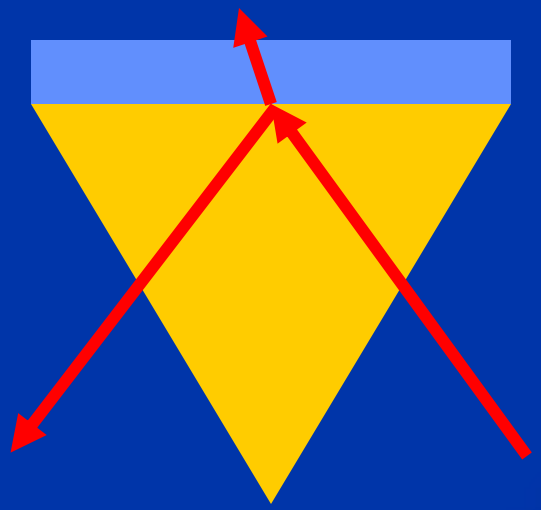
ATR Sampling – Critical Angle



$$\theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right)$$

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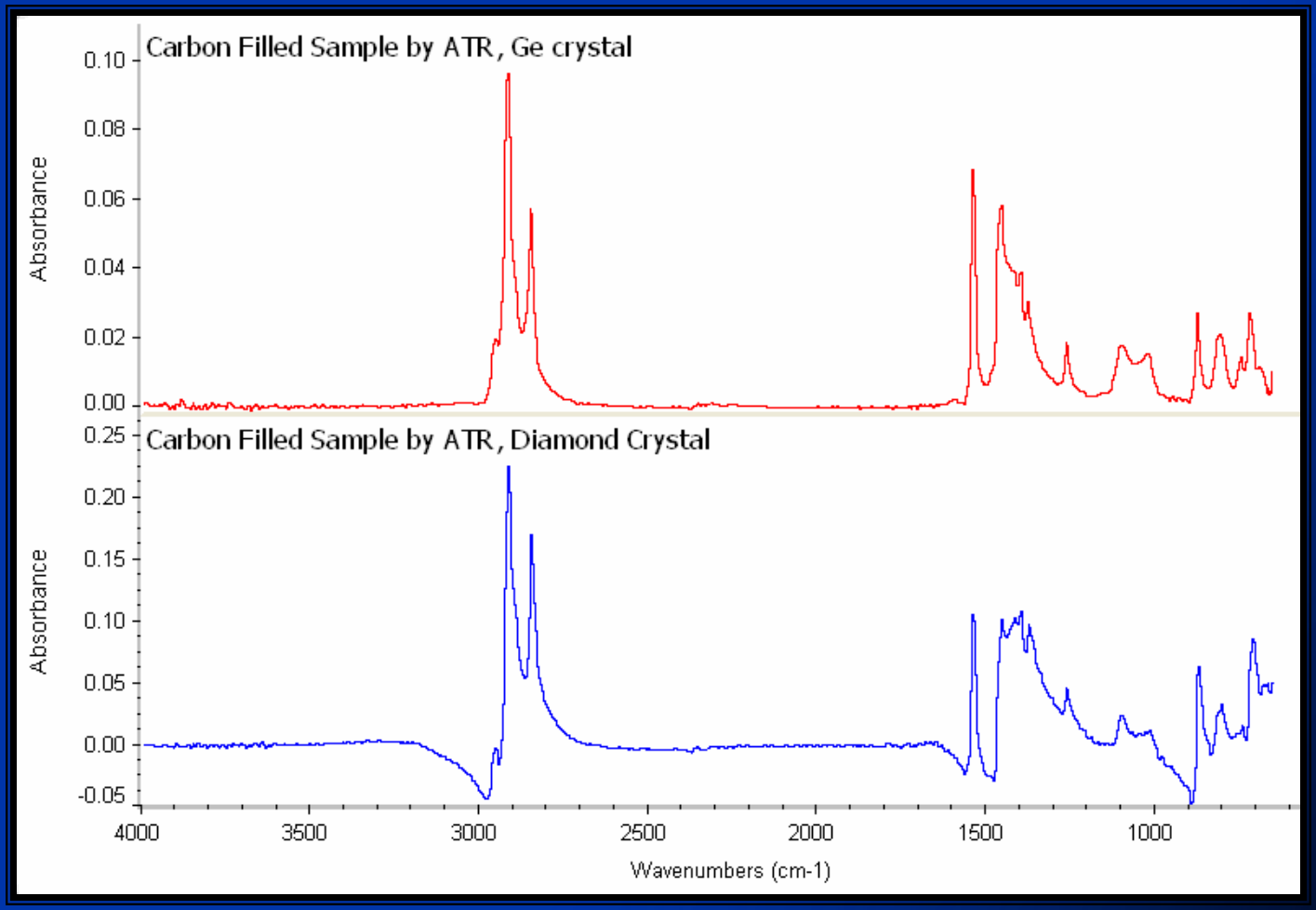
Diamond is Not Universal



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Spectroscopic Creativity

Crystal Options for MIRacle

MIRacle Crystal Plate *Application*	Hardness kg/mm^2	LWL, cm-1	Refractive Index	Depth of Penetration @ 45°, 1000 cm-1, µ	Safe pH Range
AMTIR *Harder than ZnSe, ok with acidic samples*	170	630	2.5	1.70	1 -9
Diamond / KRS-5 *When you need full mid-IR spectral range*	5700	250	2.4	2.00	1 - 14
Diamond / ZnSe *Ideal for hard samples, acids or alkaline*	5700	525	2.4	2.00	1 - 14
Ge *General purpose and carbon filled samples*	780	570	4.0	0.66	1 - 14
Si / ZnSe *General purpose - only below diamond for hardness*	1150	550	3.4	0.85	1 - 12
Si *Excellent for far-IR spectral measurement*	1150	1500, 40	3.4	0.85	1 - 12
ZnSe *General purpose ATR sampling*	120	525	2.4	2.00	5 - 9

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Spectroscopic Creativity

Single Vs Multi Reflection ATR

Single Reflection

- Qualitative, quantitative analysis – higher concentration components, >1%
- Higher throughput – faster analysis
- Wider spectral range

Multi Reflection

- Qualitative, quantitative analysis – lower concentration components, <1%
- Lower throughput – longer analysis time
- Reduced spectral range

PIKE TECHNOLOGIES

Spectroscopic Creativity

VeeMAX II with ATR – depth profiling studies & monolayers on Au, Si

- Variable angle, single-reflection HATR
- 30 to 70 degrees angle of incidence
- 0.5 to 46 micron depth of penetration
- High throughput ATR crystals
- Automated version available

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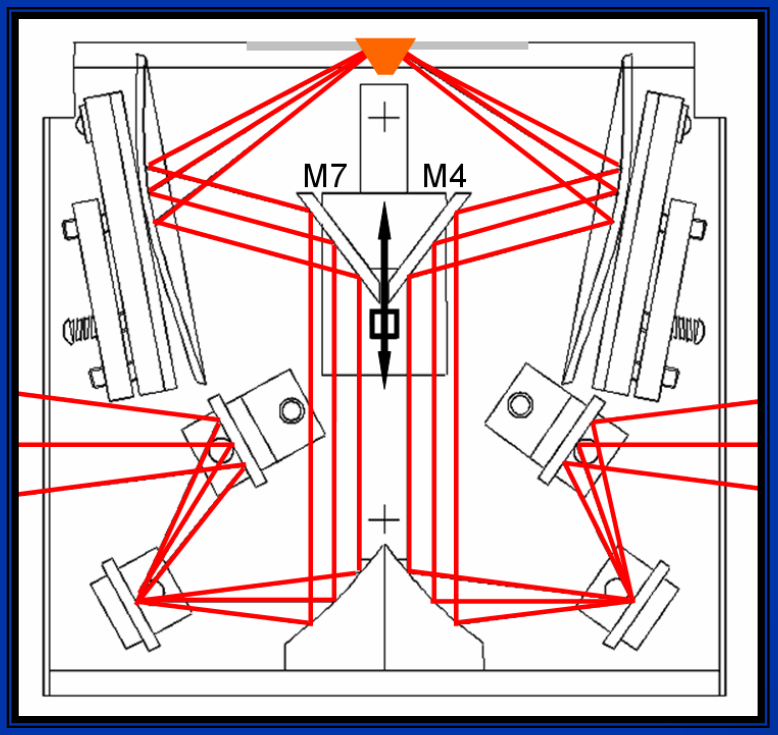
Spectroscopic Creativity

VeeMAX II with ATR – optical geometry

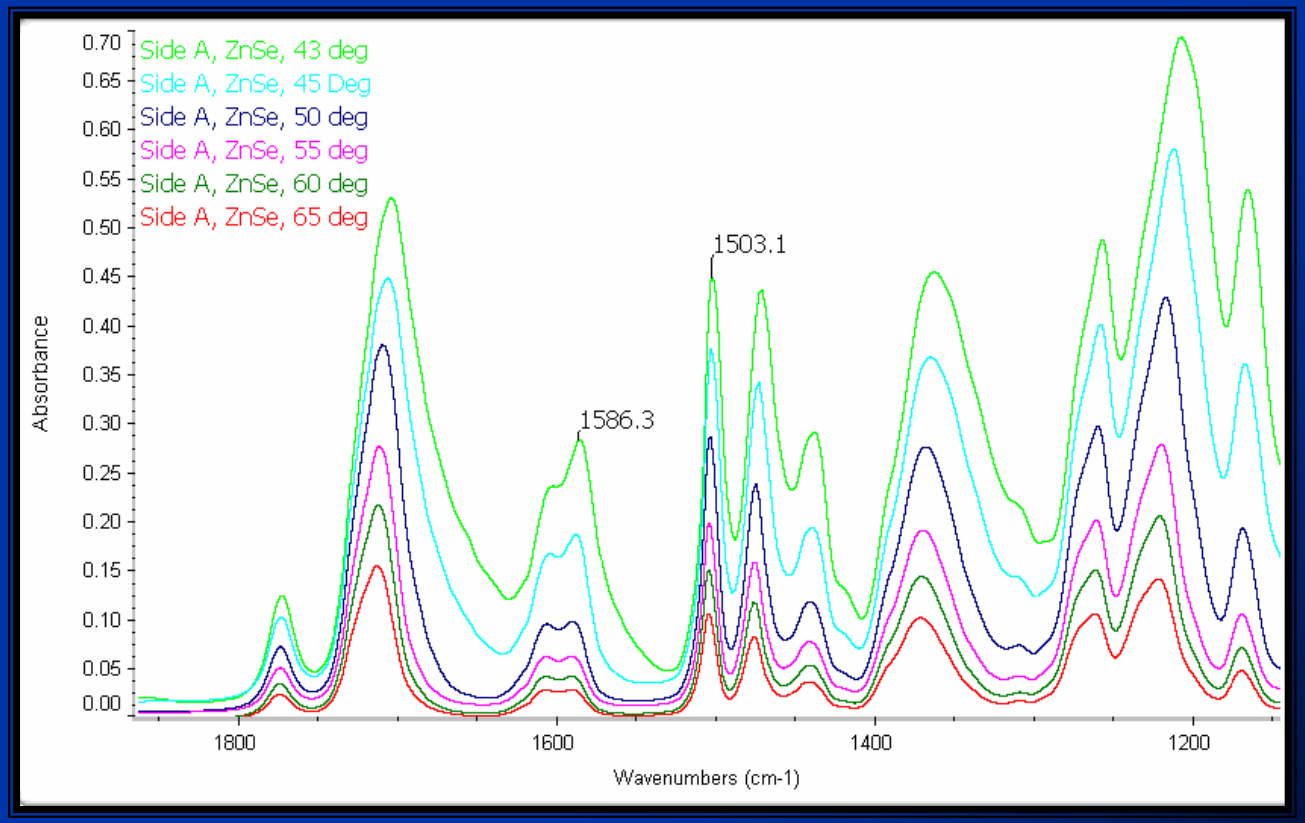


- Single selection knob – from 30 to 80 degrees set point
- No alignment required
- Available 45, 60 and 65 degree face angle crystals
- Patented optical design, PIKE Technologies

PIKE TECHNOLOGIES

Spectroscopic Creativity

ATR Depth Profile Spectral Data – *probing the sample*



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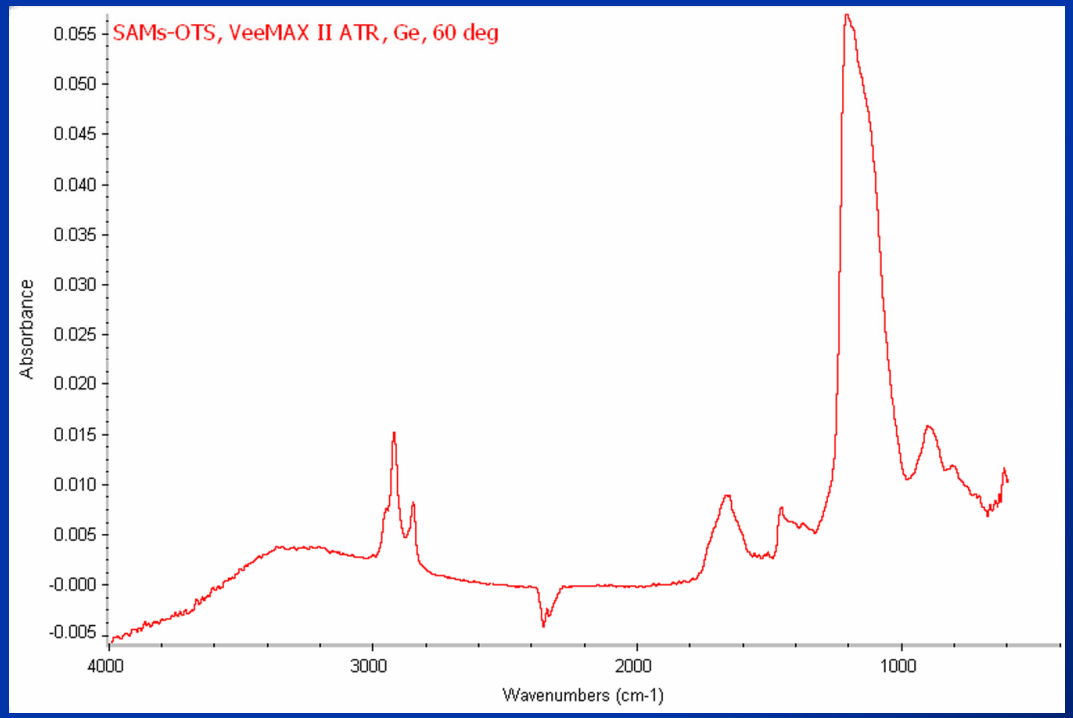
Grazing Angle ATR – Monolayers on Reflective Surfaces



- 4 min. sample and background spectra
- 60 degree Ge ATR crystal
- 4 cm-1 spectral resolution
- DLaTGS detector

PIKE TECHNOLOGIES

Spectroscopic Creativity

Diffuse Reflectance Samples & Applications

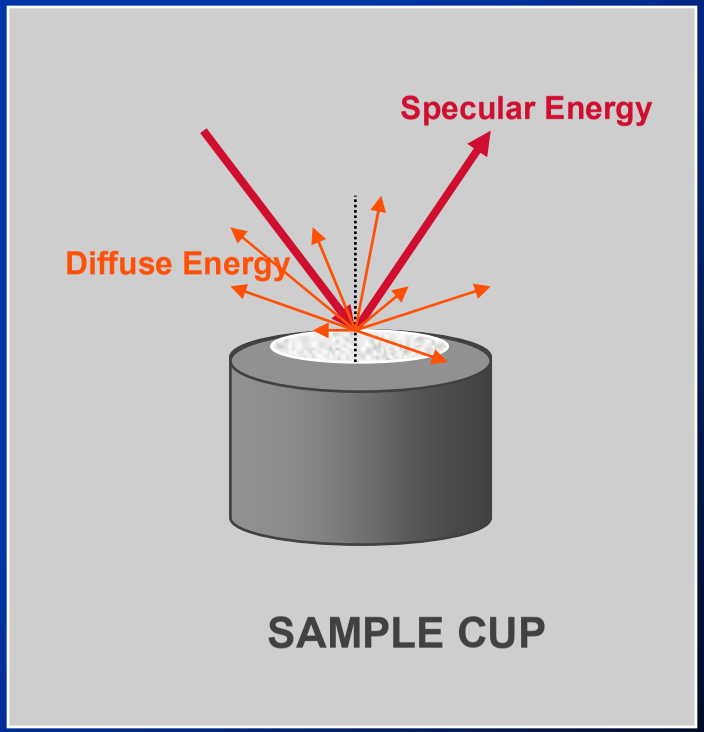
- Solid samples
- Powders
- Rough surface solids
- Coated materials
- Eliminates making KBr pellets
- Very sensitive sampling technique
- Temperature and catalytic studies

PIKE TECHNOLOGIES

Spectroscopic Creativity

Basic Theory

- IR radiation is reflected , absorbed, scattered and transmitted by the sample
- Diffusely reflected light is collected by the accessory optics and directed onto the spectrometer detector
- Only radiation that is scattered within the sample and returned to the surface is collected

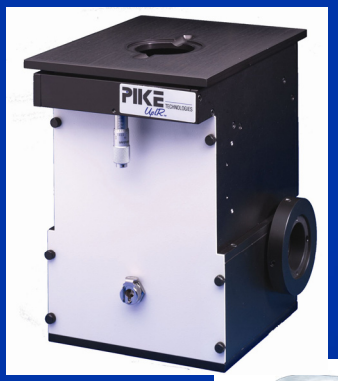


PIKE TECHNOLOGIES

Spectroscopic Creativity

Diffuse Reflectance

- DiffusIR™ – Research Diffuse Applications & Heat Chambers
- EasiDiff ™ – Workhorse Diffuse Sampling
- UpIR ™ – Upward Looking for Large Samples
- AutoDiff ™ – Unattended Powders Sampling
- X, Y Autosampler – Microtiter Diffuse Format



PIKE TECHNOLOGIES

Spectroscopic Creativity

Spectral conversions

The reflectance of a sample is related to concentration by the Kubelka-Munk equation:

$$f(R) = (1 - R)^2 / 2R = 2.3\ ac/s$$

Where: R = absolute reflectance of the layer

a = absorptivity

c = concentration

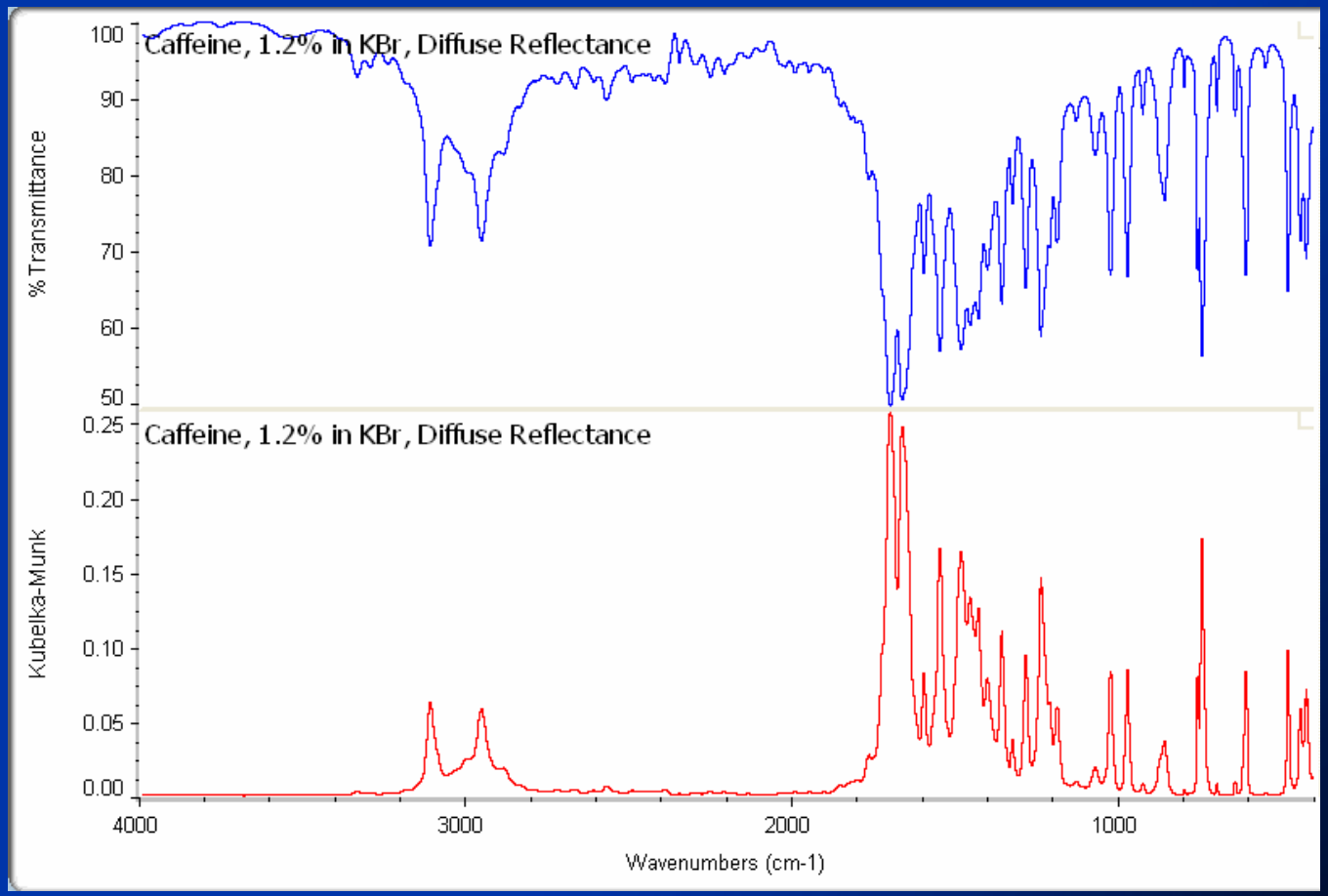
s = scattering coefficient

s depends upon particle size & sample packing - sample preparation

PIKE TECHNOLOGIES

Spectroscopic Creativity

Spectral conversions (IV)



Original and KM converted spectrum

PIKE TECHNOLOGIES

Spectroscopic Creativity

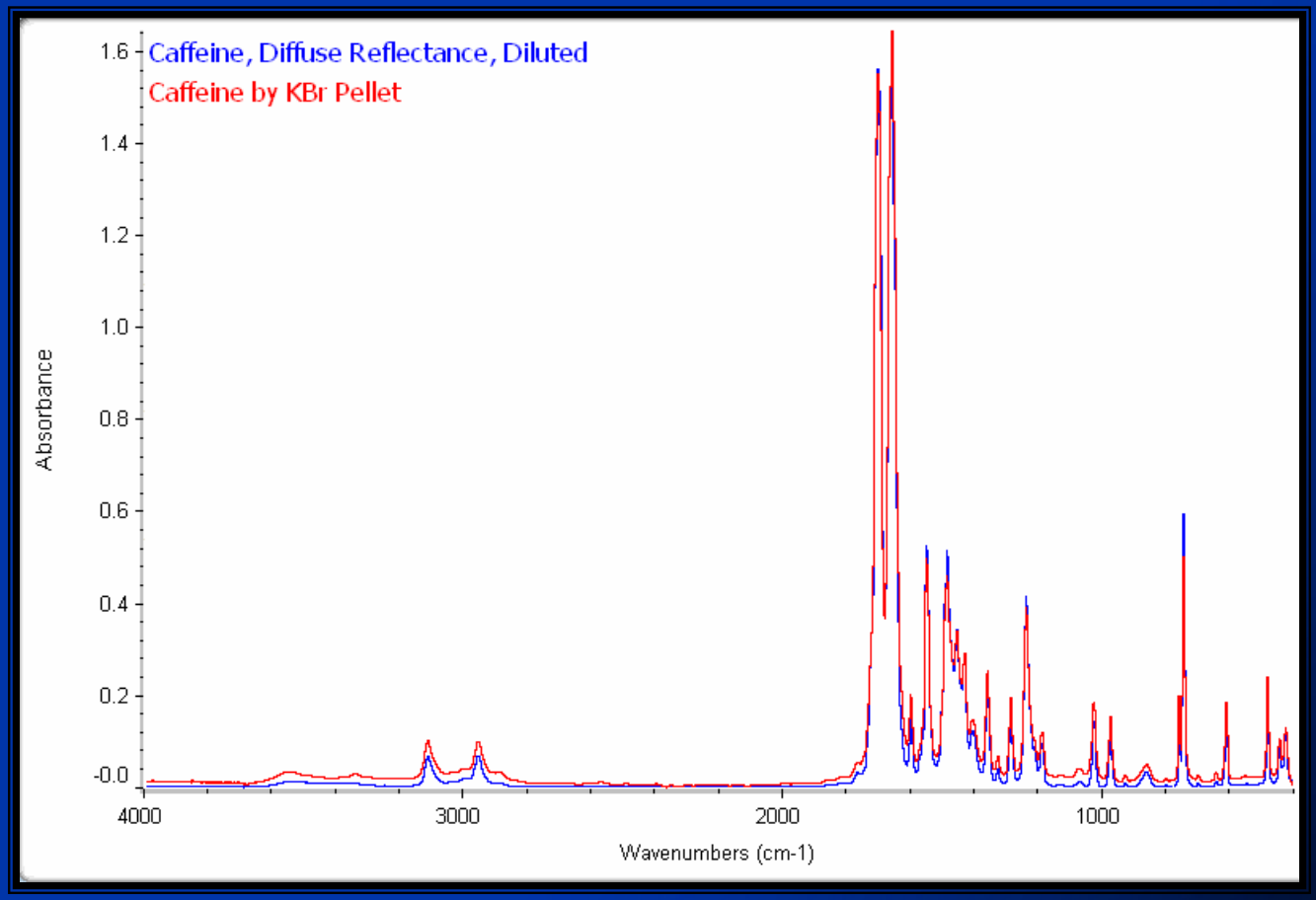
Sample Preparation

- Weigh or measure sample / matrix to achieve 1-5% mixture
- Grind (mortar and pestle) until the particle size and consistency approaches that of fine flour
- Wig-L-Bug – best result, most efficient

PIKE TECHNOLOGIES

Spectroscopic Creativity

Diffuse Reflectance Vs. Transmission Data



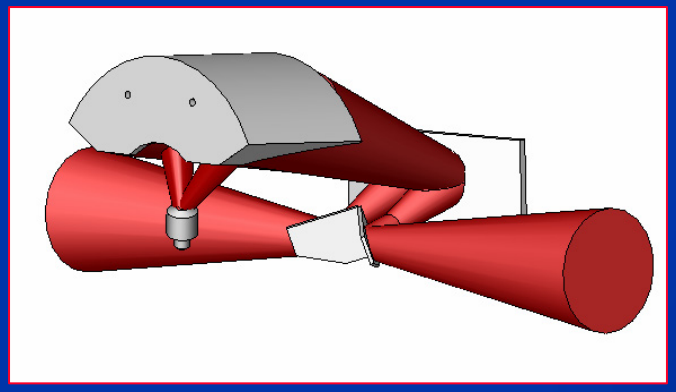
Well prepared diffuse reflectance sample – compares very well with transmission spectral data

PIKE TECHNOLOGIES

Spectroscopic Creativity

DiffusIR Heat Chambers

- 500 C and 900 C versions
- Vacuum to 1 x 10^{-6} Torr
- High pressure versions
- Pressure to 1500 psi
- Easy pin-mount insertion and removal

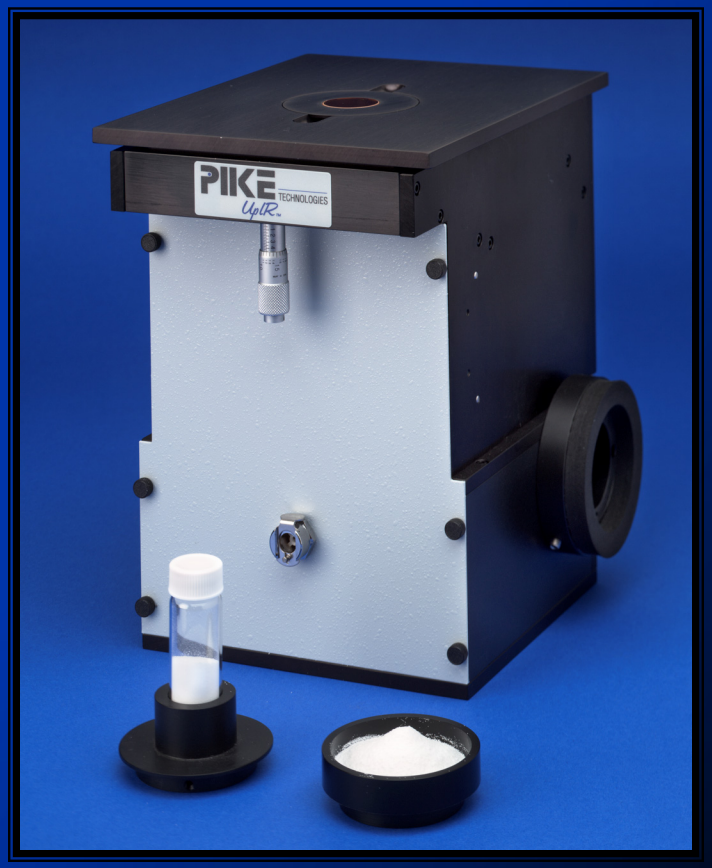


PIKE TECHNOLOGIES

Spectroscopic Creativity

UpIR™ Diffuse Reflectance

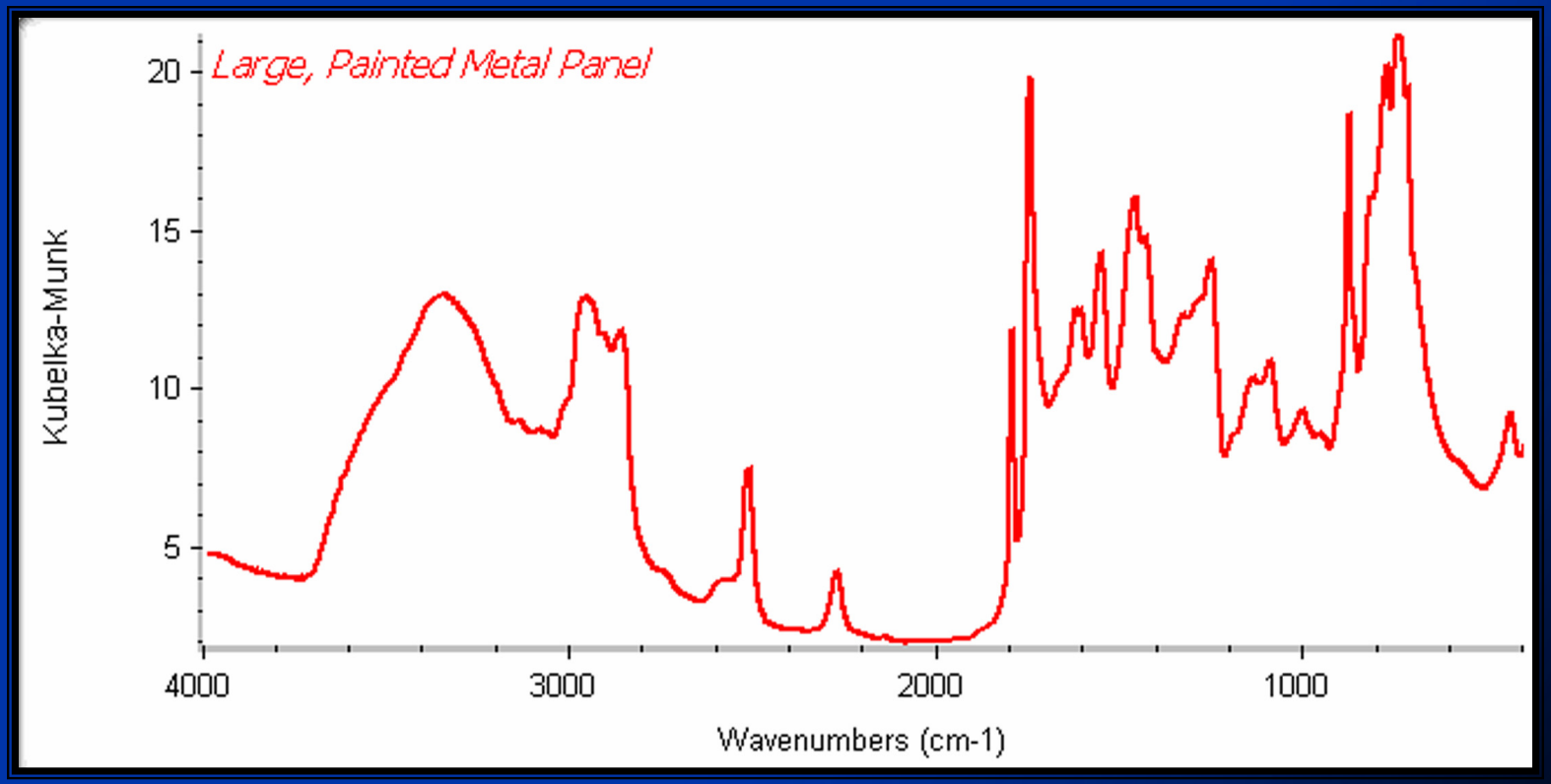
- Out-of-compartment , upward looking diffuse reflectance accessory
- Powdered samples, large samples
- No purge loss with sample exchange
- NIR and mid-IR configurations
- Permanently mounted optical components
- Micrometer sample focus
- Excellent performance



PIKE
TECHNOLOGIES

Spectroscopic Creativity

UpIR Spectral Data



- Sample face down on UpIR, reference gold mirror

PIKE TECHNOLOGIES

Spectroscopic Creativity

Specular Reflection Appplications

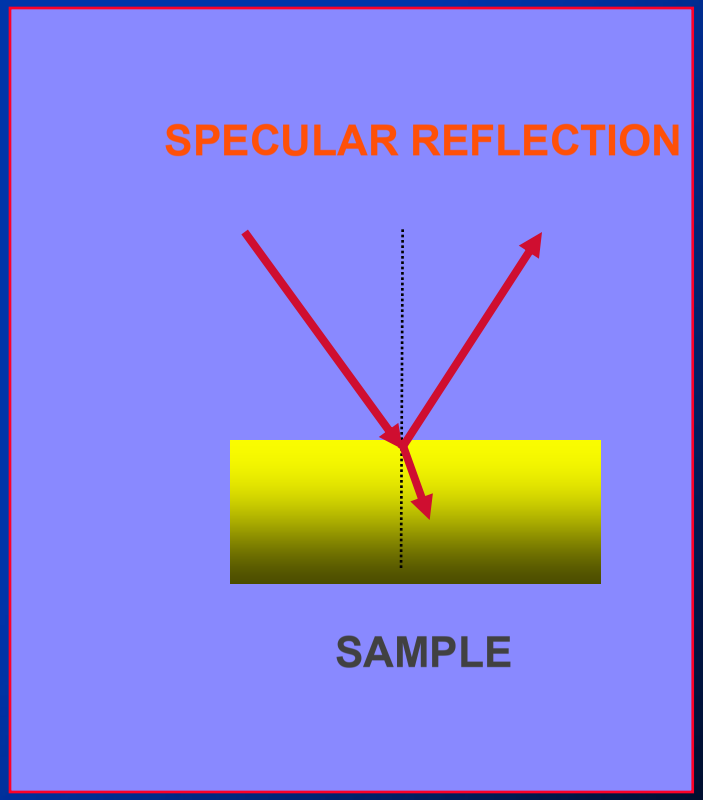
- Measure thin films on metallic substrates
- In situ analysis of bulk materials
- Characterization of non IR transmissive samples
- Measure thickness of free standing transmitting films

PIKE TECHNOLOGIES

Spectroscopic Creativity

Basic Theory

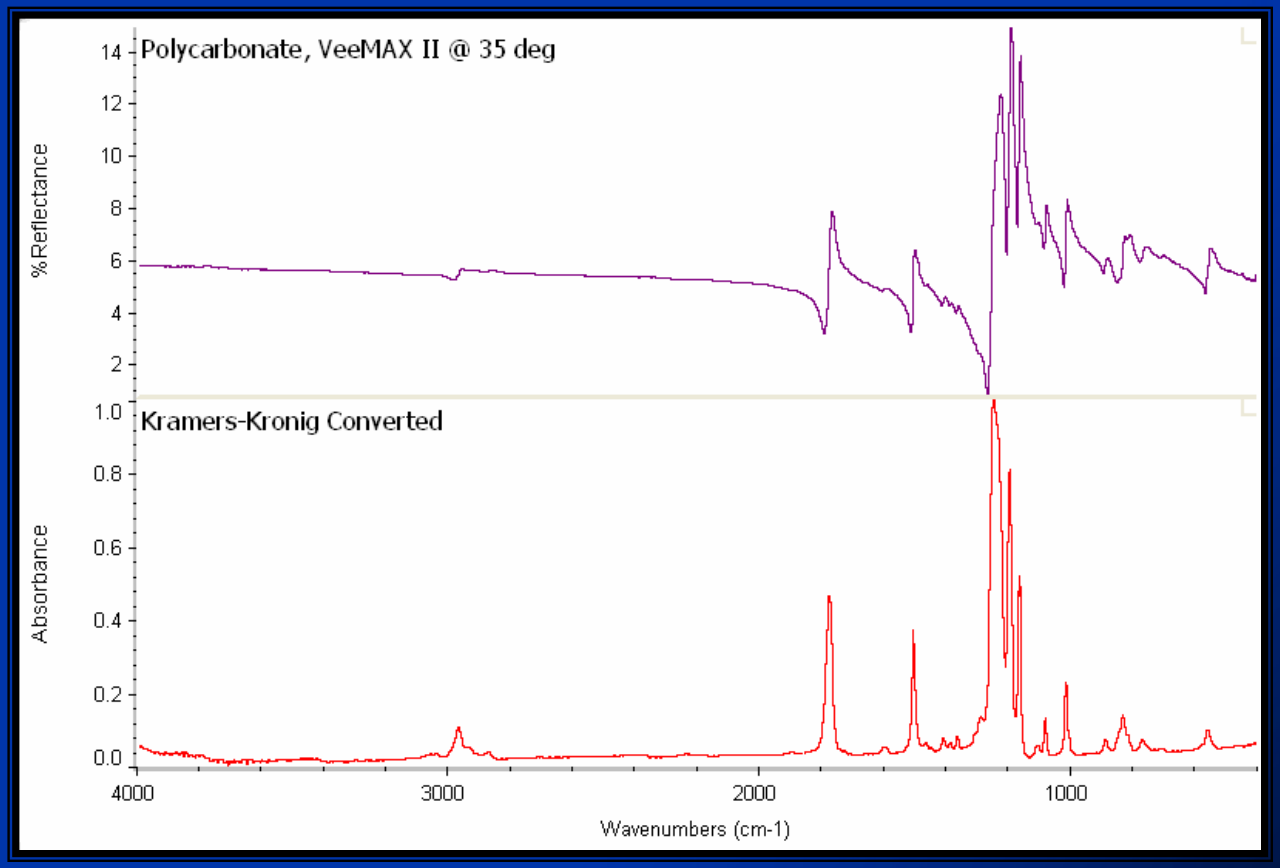
- Mirror-like reflection of the IR energy from the surface of the sample
- Radiation intensity depends on angle of incidence, index of refraction, absorption properties and surface of the sample.



PIKE TECHNOLOGIES

Spectroscopic Creativity

Analysis of Bulk Materials

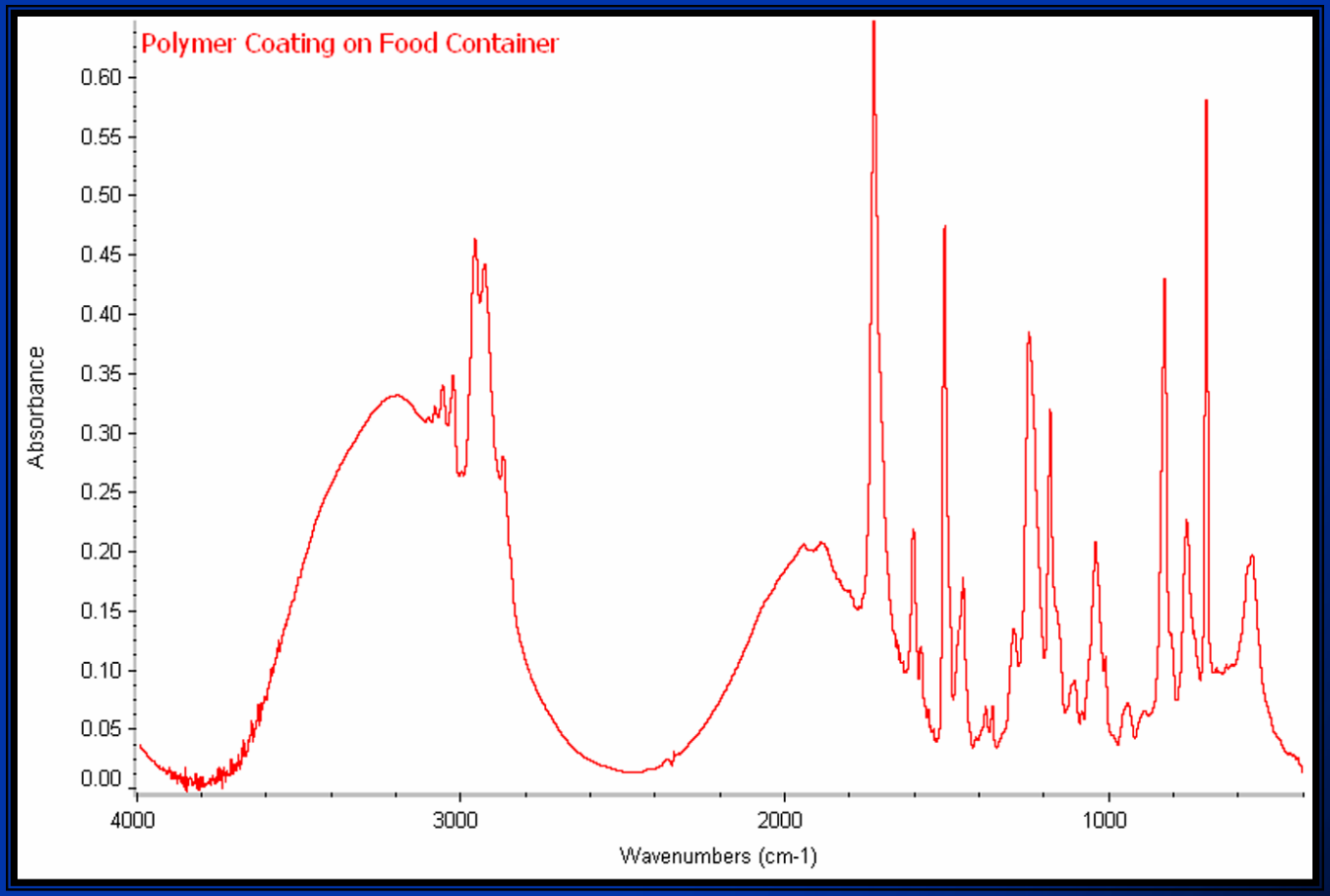


- Specular reflection spectrum shows dispersion at absorbance bands – due to real and imaginary refractive index components
- Kramers-Kronig transformation is used to convert them to absorbance like spectrum

PIKE TECHNOLOGIES

Spectroscopic Creativity

Thin Coatings on Reflective Substrates



- Sample face down on 30Spec – no sample preparation
- Excellent quality spectra of coatings on reflective substrates
- Identified as a polyvinyl ester

PIKE TECHNOLOGIES

Spectroscopic Creativity

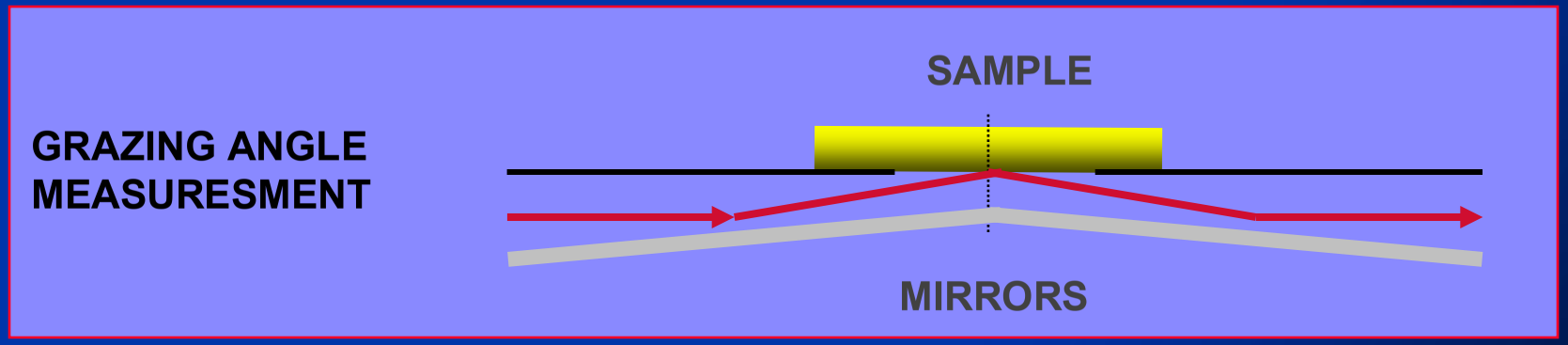
Grazing Angle Specular Reflectance Applications

- 65 - 85 degree angle of incidence
- Very thin films on reflective surfaces
- Molecular orientation studies
- Measurements of samples at nanometer thickness

PIKE TECHNOLOGIES

Spectroscopic Creativity

Basic Theory

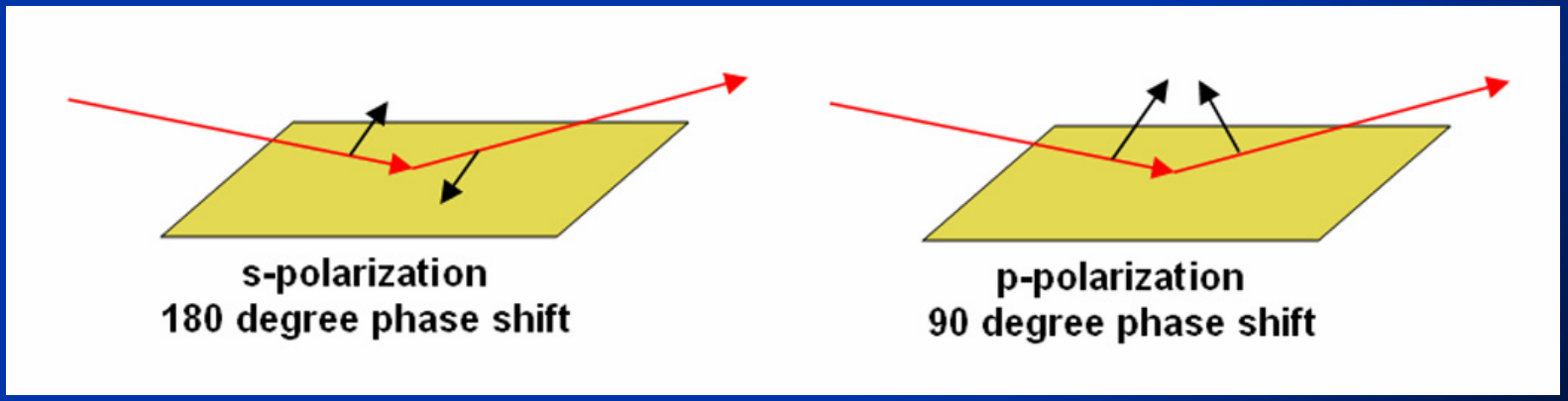


- Most sensitive for films less than 1/4 of the wavelength thickness - interaction of the sample and beam electromagnetic fields at that distance
- Orientation studies use “p” polarized light to enhance measurement sensitivity

PIKE TECHNOLOGIES

Spectroscopic Creativity

Grazing Angle, Polarization Effect

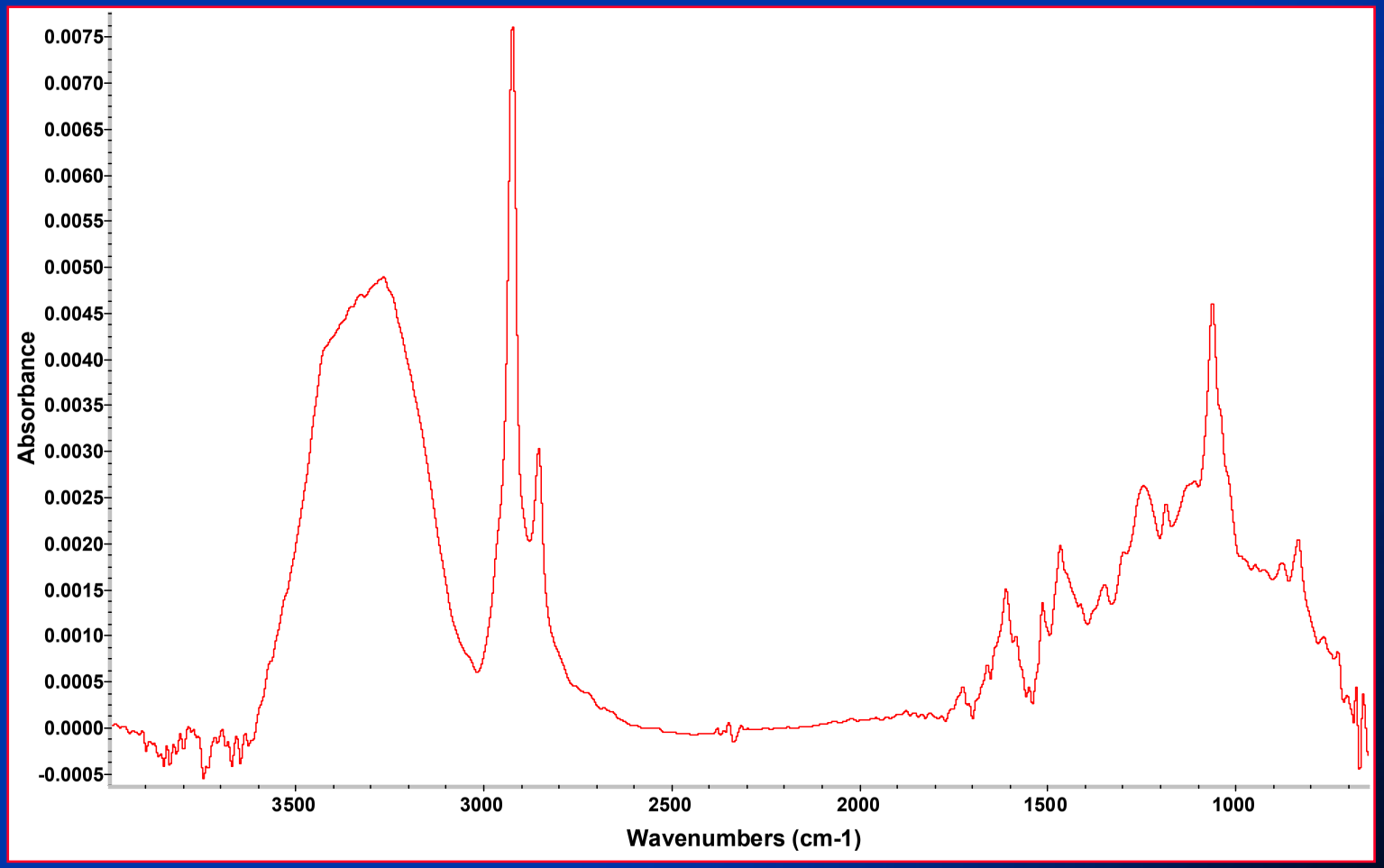


- S-polarized beam phase shift causes cancellation of electric field intensity at sample surface
- P-polarized beam phase shift produces additive effect of electric field intensity at surface

PIKE TECHNOLOGIES

Spectroscopic Creativity

VeeMAX Applications



- Thiol monolayer on Au
- VeeMAX @ 80 deg AOI, p-polarization, MCT detector, 4 cm-1 resolution, 1 minute background and sample

PIKE TECHNOLOGIES

Spectroscopic Creativity

Summary – Modern FTIR Sampling Techniques

- PIKE Technologies offer a complete line of FTIR accessories
- ATR, Diffuse Reflectance and Specular Reflectance can greatly speed and simplify FTIR analysis
- Awareness of the optimal sampling technique often makes the analysis possible

PIKE TECHNOLOGIES

Transmission Sampling Techniques – *Theory and Applications*

FTIR sampling by transmission is a very popular method for collection of infrared spectra. Its use is easy to explain – the methods are intuitive and do not require sophisticated sampling accessories. In many cases, the sample can be placed directly into the path of the infrared beam (with the help of sample holder) and scanned. Further benefits of transmission sampling techniques include compatibility with automated sampling and microsampling techniques such as IR Microscopy.

Transmission techniques are well documented and have been successfully used for many years. A large number of spectral libraries contain transmission spectra and are often used as references for the purpose of qualitative analysis. Transmission techniques offer many advantages and should be used whenever possible, unless reliable sample preparation becomes too difficult, too time consuming or impossible. Transmission is also widely used for quantitative applications, as significant numbers of basic measurements adhere to the Beer-Lambert law. The law provides a mathematical relationship between the infrared radiation absorbed by the sample and the sample concentration:

$A = a \cdot b \cdot c$

Where:

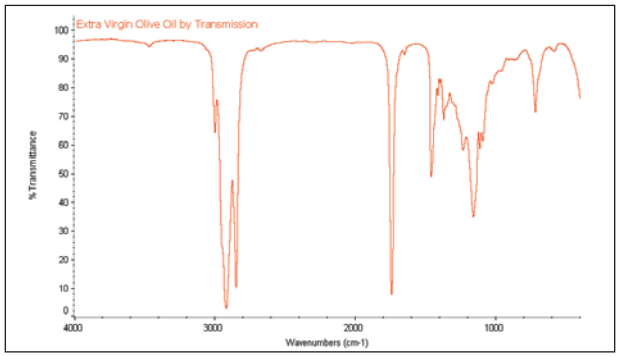
A = absorbance
a = absorptivity
b = path length
c = sample concentration

The Beer-Lambert law states that absorbance is linearly proportional to sample concentration (with sample path length and absorptivity constant). The actual measurements are generated in percent transmittance (which is not a linear function of concentration), however, they can be converted in real time to absorbance by all modern FTIR instrumentation. As mentioned before, transmission measurements are intuitive and simple. However, the majority of samples are too thick to be measured directly and they have to be processed in some way before meaningful data can be collected. Some of the sample preparation techniques are time consuming and can be destructive. Liquids and pastes are generally the easiest samples to run. A large number of liquid cells and windows are available for liquid measurements. Solid samples (with the exception of thin films) require sample preparation – making a pellet (typically potassium bromide – KBr) or a mull. Gas samples require a suitable gas cell with a pathlength sufficient to detect the desired component.

Sample Preparation and Analysis

Liquids

Most liquids and dissolved solids are easy to measure by transmission. Viscous liquids or pastes can be simply pressed between 2 IR transparent windows and measured by FTIR.



FTIR Spectrum of 1 drop of Extra Virgin Olive Oil pressed between 25 mm KBr windows and held in the IR beam using the PIKE Universal Sample Holder.

Thin liquids or samples in solvent may be best run by using a demountable liquid cell or a sealed cell, consisting of two windows with a precision spacer in-between. One of the windows has two drilled holes for the introduction and evacuation of the sample. A large number of cell options are available – these include permanently sealed cells, demountable cells with different window materials and a wide selection of spacers.

The pathlength of liquid cells can be easily measured with your FTIR spectrometer. Just place the empty cell into the FTIR and collect its spectrum. The frequency of the sine wave spectrum (produced by back reflection within the cell) provides the pathlength using the following equation;

$P = (10 \cdot N) / (2 \cdot \Delta\ cm^{-1})$

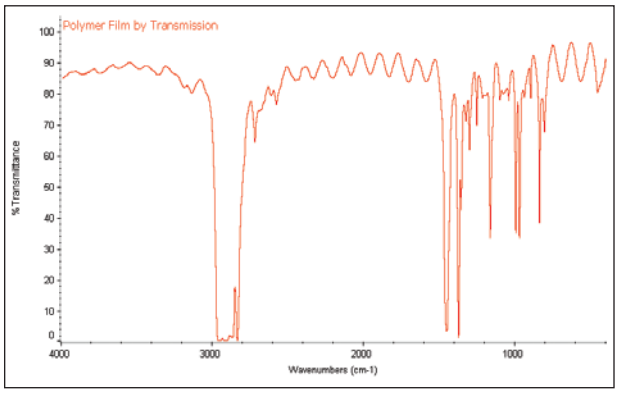
Where:

P = pathlength of cell in mm
N = number of fringes within $\Delta\ cm^{-1}$
$\Delta\ cm^{-1}$ = wavenumber range of fringe count

It is very important to select compatible IR transparent windows for your liquid samples. Please refer to the chart on the last page of this note to select your windows. If you still have questions, please call us.

Solids

The easiest to analyze are film and polymer samples less than 200 micrometers thick (ideal thickness for the major component of a polymer film is about 20 microns). These samples can be simply placed into a sample holder and immediately scanned.



Polymer Film from Product Packaging Material – held in place with the PIKE Universal Sample Holder. Polymer is identified as Atactic Polypropylene and the film is determined to be 27.1 microns thick.

The thickness of the polymer film can be calculated from the fringe pattern in the spectrum using the following equation;

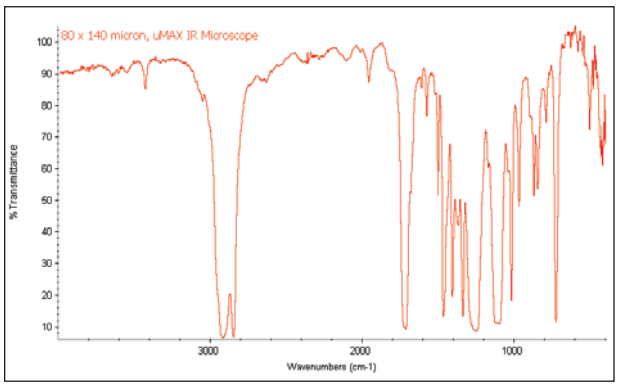
$T = (10000 \bullet N) / (2 \bullet n \bullet \Delta\ cm^{-1})$

Where:

T = thickness of polymer film in microns
N = number of fringes within $\Delta\ cm^{-1}$
$\Delta\ cm^{-1}$ = wavenumber range of fringe count
n = refractive index of polymer

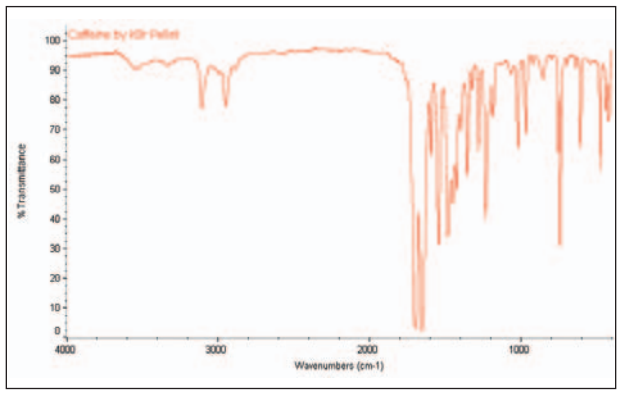
The same procedure can be used for samples which can be sliced and pressed to an appropriate thickness – especially for IR microsampling.

For IR microsampling, one can place a small sliced sample into a sample compression cell and apply pressure to hold the sample and to thin it to a useable thickness – as shown in the following spectral data.



Micro Spectrum of a Layered Polymer using a PIKE µMAX IR Microscope and Compression Cell with KBr windows.

However, the majority of solid materials must be prepared before their infrared spectra can be collected. In many cases sample preparation involves grinding of the sample and mixing it with an IR transparent material such as KBr and then pressing a pellet. While this method of solids analysis is time consuming, it produces an excellent result.

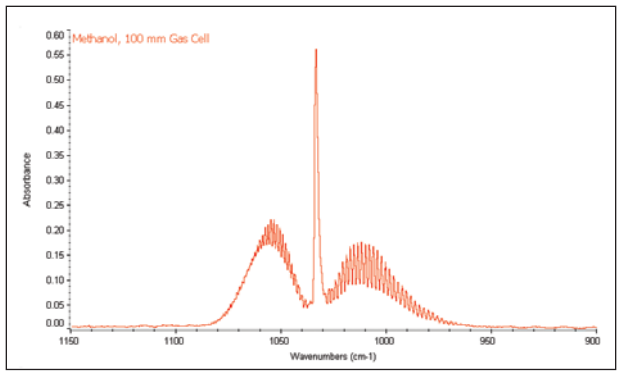


FTIR Spectrum of Caffeine prepared as a 13 mm KBr Pellet and held in position with the PIKE Sampling Card.

Solid Sample Preparation Tips

The best method for preparation of solid samples involves mixing the sample (about 5% by weight) with an IR transparent material (typically KBr) and pressing a pellet. The mixing is best done with a Wig-L-Bug accessory which produces a fully mixed and pulverized sample in about 30 seconds. The mixing can also be done with a mortar and pestle – but not as well. Generation of a pellet involves pressing the prepared mixture with a hydraulic or hand press into a hard disk. The pellet, ideally 0.5 to 1 mm thick is then placed in a transmission holder and scanned. Typically, the pellet technique provides good quality spectra with a wide spectral range and no interfering absorbance bands.

Samples which do not grind well and/or are affected by solvents and mulling agents can be analyzed with high pressure techniques. Typical samples include fibers and paint chips. The accessory used for such applications utilizes two diamond anvils. Difficult samples are placed between the diamonds and crushed, compressed and flattened to the thickness necessary to obtain good quality FTIR spectra. Diamond cells are transparent to IR radiation except in the region of 2400 cm^{-1} to 1700 cm^{-1}. The high pressure diamond cells require the use of a beam condenser or an infrared microscope.



FTIR Spectrum of Methanol Vapor measured with the PIKE 100 mm gas cell using 0.50 cm^{-1} spectral resolution.

An alternate method for analysis of solid materials involves making a mull. Mulls are sample suspensions in Nujol (refined mineral oil) or Fluorolube (perfluorohydrocarbon). The process is based upon mixing 1 to 2 drops of the mulling agent with a ground sample until a uniform paste is formed. The paste is transferred onto a KBr or other IR transparent disk, placed in the sample compartment of the spectrometer and scanned. The advantage of this technique is that it is a relatively quick and simple procedure; disadvantages include interference from mulling agent absorption bands. (Both Nujol and Fluorolube have characteristic spectral features and in most cases have to be used as a pair in order to generate a complete mid IR spectrum. Nujol is used below 1330 cm^{-1}, Fluorolube above 1330 cm^{-1}).

Gases

Analysis of gas samples is a unique form of transmission sampling by FTIR as the identified sample does not need to be of pure composition. At high spectral resolution, most gas mixtures can be identified and quantified since absorbance bands can be selected within the spectrum, which are resolved and distinct from other components within the sample.

Simple demountable cells (50 mm to 100 mm) are recommended for samples in a 1 – 10% by weight concentration range.

For highly dilute samples (ppm to ppb concentrations), long path cells are required. The long path cell reflects the IR beam several times through the sample using a set of mirrors positioned on the opposite ends of the cell, producing a pathlength to 10 to 30 meters – or more. It is important to select window materials compatible with the investigated sample. Gas sampling accessories can be fitted with different windows to accommodate the physical and chemical characteristics of the measured gas. Special designs for high pressure and temperature controlled experiments are also available.

Summary

Transmission sampling by FTIR provides an excellent means for sample identification and quantification of sample components. Most samples measured by transmission techniques require some sample preparation, however, the quality of the results and amenability to automation and microsampling offer significant advantages.

Properties of Select Infrared Transmitting Materials For Transmission Spectroscopy

Material	Comments	SWL cm^{-1}	LWL cm^{-1}	RI	Solubility G/100g	Hardness Kg/mm^2	MP °C	pH Range
AMTIR	GeAsSe glass, brittle	11000	593	2.50	0.00	170	370	1 – 9
BaF_2	Barium Fluoride	66600	691	1.45	0.17	82	1280	5 – 8
CaF_2	Calcium Fluoride	79500	896	1.40	0.0017	158	1360	5 – 8
CsI	Cesium Iodide, very hygroscopic, Somewhat Toxic	42000	172	1.73	44	20	621	NA
Diamond	Type IIa, strong IR absorbance between 2700-1800 cm^{-1}, costly	30000	<2	2.40	0.00	5700	550 flash point	1 – 14
Ge	Germanium, brittle, becomes opaque at elevated temperatures	5500	432	4.00	0.00	780	936	1 – 14
KBr	Potassium Bromide, most widely used for mid-IR applications	48800	345	1.52	53	6	730	NA
KCl	Potassium Chloride	55600	385	1.45	35	7	776	NA
KRS-5	Thallium Bromide/Thallium Iodide, Extremely Toxic!	17900	204	2.37	0.05	40	414	5 – 8
NaCl	Sodium Chloride	52600	457	1.49	36	18	801	NA
Polyethylene	For Far-IR, swells with some organic solvents	625	<4	1.52	0.00		110	1.5 – 14
SiO_2	Silicon Dioxide	50000	2315	1.53	0.00	460	1713	1 – 14
Si	Silicon, strong IR absorbance between 624-590 cm^{-1}	8900	624, 30	3.41	0.00	1150	1420	1 – 12
ZnS	Zinc Sulfide	17000	690	2.20	0.00	240	1830	5 – 9
ZnSe	Zinc Selenide	15000	461	2.40	0.00	120	1526	5 – 9

Notes: The above table is meant to be a general guide – brief and concise. For more information about these materials, consult appropriate reference books and Material Safety Data Sheets (MSDS).

SWL – Shortest wavelength for transmission, 1 mm, 50% transmission

LWL – Longest wavelength for transmission, 1 mm, 50% transmission

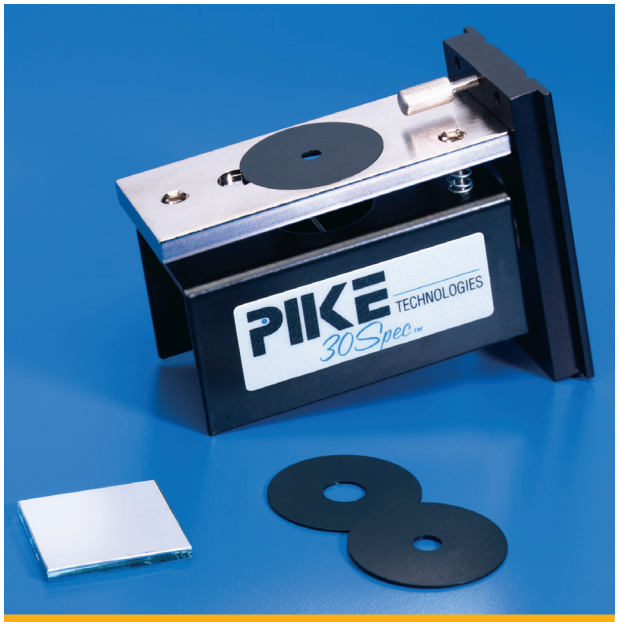
RI – Refractive Index, at relevant wavelength

MP – Melting point

PIKE TECHNOLOGIES

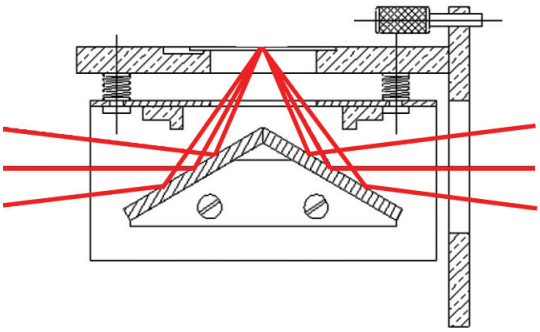
2901 Commerce Park Drive Madison, WI 53719-5120 • (608) 274-2721 • (608) 274-0103 (FAX) • www.piketech.com • sales@piketech.com (E-MAIL)

30Spec – *Specular Reflectance for Relatively Thick Films*



FEATURES OF THE 30SPEC

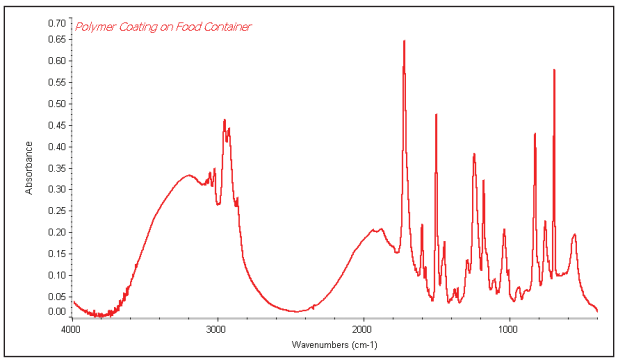
- *Measurement of relatively thick films*
- *Measurement of film thickness by specular reflectance*
- *Fixed 30 degree angle of incidence*
- *Sample masks to define sampling area*
- *Special version – 45Spec for fixed 45 degree angle of incidence*
- *Slide mount design for easy installation of accessory – fits all FTIR spectrometers*



Optical geometry for the 30Spec

The PIKE Technologies 30Spec™ is ideal for the measurement of relatively thick films by specular reflectance. Samples are simply laid across the top of the accessory and the spectrum of the film is measured within a short time period. The 30Spec includes sample masks of 3/8", 1/4" and 3/16" to define specific sampling areas. The 30Spec provides high quality FTIR spectra for identification of coatings and can also be used to measure coating thickness.

IR throughput is high using the 30Spec due to the relatively simple optical design of the product.



FTIR spectrum of polymer coating on a food container run with the PIKE 30Spec

ORDERING INFORMATION

30Spec and 45Spec Accessory

PART NUMBER	DESCRIPTION
011-1000	30Spec – Specular Reflectance Accessory (30 degree) *Includes sample masks (3/8", 1/4", and 3/16"), alignment mirror and slide mount.*
011-4500	45Spec – Specular Reflectance Accessory (45 degree) *Includes sample masks (3/8", 1/4", and 3/16"), alignment mirror and slide mount.*

Notes: The 30Spec and 45Spec are slide mount accessories.

30Spec and 45Spec Sampling Options

PART NUMBER	DESCRIPTION
011-2010	Sample Masks (3/8", 1/4", and 3/16")
300-0039	Alignment Mirror

Notes: Sample masks and alignment mirror fit 30Spec and 45Spec.

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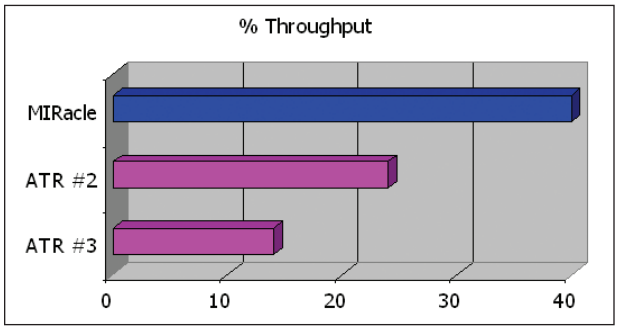
MIRacle ATR – *Fast and Easy IR Sampling*

FEATURES OF THE MIRACLE

- *Highest IR throughput – saving you time and improving your analysis quality*
- *Complete flexibility – add options to your MIRacle as your sampling needs change*
- *Highest value – for today's competitive analytical and research needs*
- *Fully configurable – ZnSe, Diamond, AMTIR, Ge and Si MIRacle crystal plates*
- *Pinned-in-place, changeable crystal plates – for fast and easy sampling optimization*
- *Highest purity, type IIa Diamond crystal – will not scratch and is chemically inert to acidic or caustic materials*
- *Optional specular reflectance plate – for measurement of coatings on reflective surfaces*
- *Choice of pressure clamps – high pressure, rotating high pressure, digital high pressure, viewing high pressure and micrometric sample clamps*
- *Sampling options – heating, temperature control, and flow through plate*

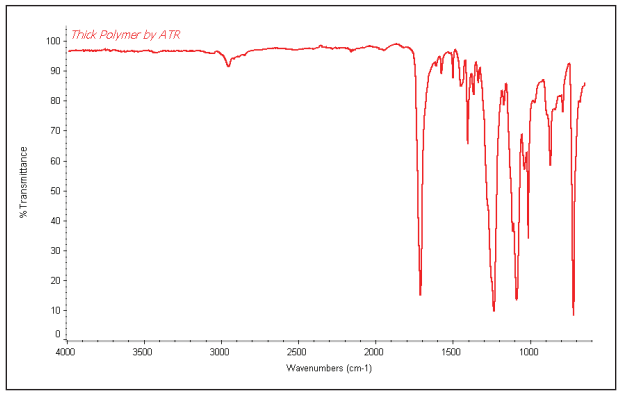


MIRacle – Highest IR Throughput ATR

The PIKE MIRacle™ is a universal ATR sampling accessory for analysis of solids, liquids, pastes, gels, and intractable materials. In its most popular configuration it is a single reflection ATR accessory with high IR throughput which makes it ideal for sample identification and QA/QC applications. Advanced options include three reflection ATR crystal plates to optimize for lower concentration components. Easily changeable crystal plate design provides analysis of a broad spectrum of sample types while ensuring constant sampling path length.

Single and three-reflection ATR crystals are available to optimize general qualitative analysis or quantitative analysis of minor components.

The PIKE MIRacle provides higher throughput – saving you time and generating higher quality spectra.



Thick Polymer Sample, using MIRacle with AMTIR Crystal and High-Pressure Clamp – No Sample Preparation.

MIRacle Optical Design

In the patented MIRacle optical design the ATR crystal both focuses the IR beam and provides the ATR sampling interface. This technology provides much higher throughput than competitive products and saves you considerable time and provides you higher quality spectra.

MIRacle – High Throughput and Efficient Optical Design

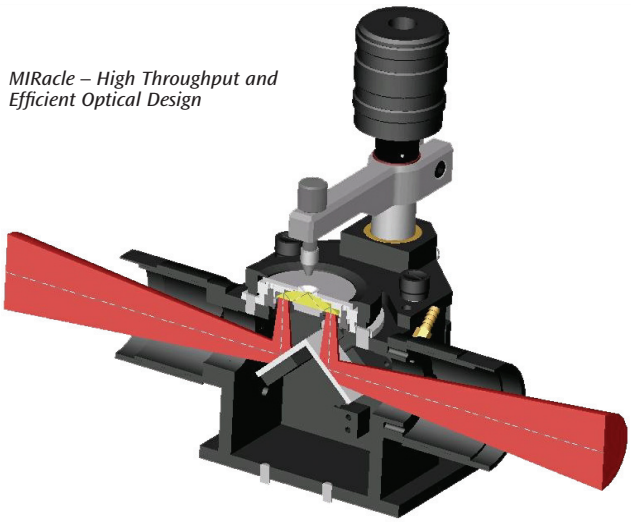


Table 1: MIRacle Crystal Plate Specifications

MIRacle Crystal Plate	Application	Hardness kg/mm²	Cutoff cm⁻¹, Spectral Range	Refractive Index @ 1000 cm⁻¹	Depth of Penetration @ 45°,µ	pH Range of Sample
AMTIR	Harder than ZnSe, ok with acid samples	170	630	2.5	1.70	1 – 9
Diamond/ZnSe	Ideal for hard samples, acids or alkaline	5700	525	2.4	2.00	1 – 14
Ge	General purpose and carbon filled or rubber	550	575	4.0	0.66	1 – 14
Si/ZnSe	General purpose – only below diamond for hardness	1150	550	3.4	0.85	1 – 12
Si	Excellent for far-IR spectral measurement	1150	8900-1500, 475-40	3.4	0.85	1 – 12
ZnSe	General purpose ATR crystal	120	520	2.4	2.00	5 – 9

MIRacle Crystal plates are covered by PIKE Technologies patent numbers 5,965,889 and 6,128,075 or are manufactured under license of 5,200,609, 5,552,604 and 5,703,366.

MIRacle Crystal Options

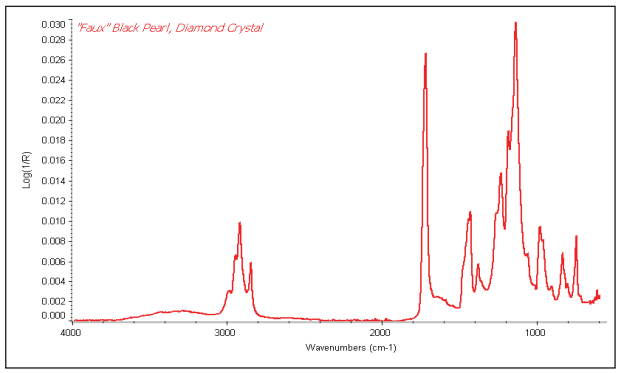
The MIRacle ATR accessory is available with 5 different crystal types (ZnSe, Diamond, Ge, Si, and AMTIR) and with unique versions of these crystal materials.

Crystal plates are pinned in place and easily changeable within seconds with no alignment required. With this flexibility, you can change the crystal type to exactly match your sampling requirements. For example, diamond is ideal for brittle samples because it will not scratch, whereas, Ge is ideal for carbon filled samples because of its high refractive index and lower depth of penetration. Three reflection crystal plates provide increased sensitivity for minor components in liquid or non-rigid materials.

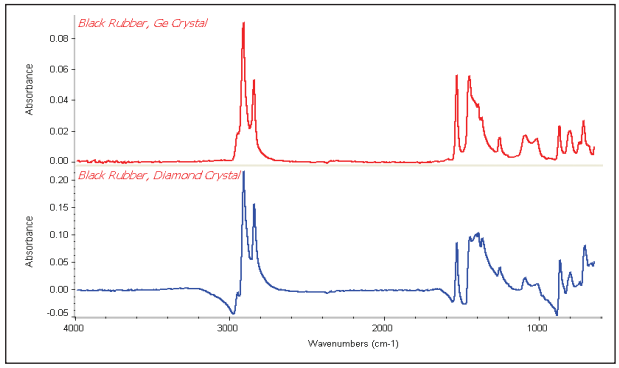
The MIRacle base optics includes a trough insert and volatiles cover, both compatible with all crystal plates – so you do not need to purchase flat and trough crystal plates.

Table 1 shows MIRacle ATR crystal characteristics including refractive index, spectral range cutoff, pH range and hardness for single reflection ATR crystal plates. *Still have questions?* Please call as we are pleased to discuss your sampling requirements.

MIRacle ATR Crystal Plates



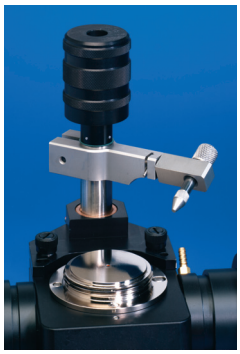
"Faux" Black Pearl with MIRacle using Diamond ATR Crystal



Black Rubber Samples are best run using Ge ATR Crystal

MIRacle Pressure Clamps are Pinned-in-Place and Easily Upgraded

MIRacle Digital Clamp *Ideal for Controlled Pressure*



MIRacle Rotating Clamp *Ideal for Cleaning Tip of Debris*

MIRacle Viewing Clamp *Ideal for Placing Fibers or Crystals*

MIRacle High-Pressure Clamp *– Ideal for Routine Sampling*

MIRacle Micrometer Clamp *– OK for Low Pressure Applications*

MIRacle Pressure Clamp Options

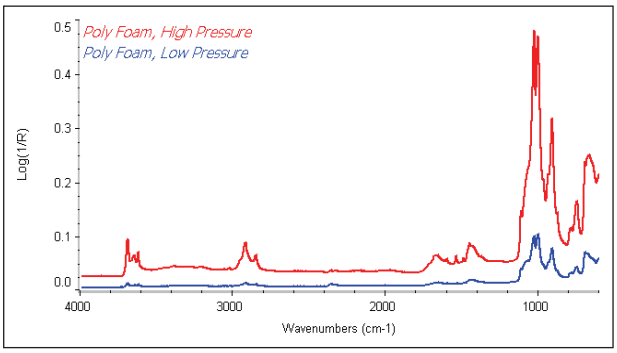
MIRacle pressure clamps are pinned in place and easily changeable within seconds. A high-pressure clamp is recommended for most applications and is available in digital, rotating and viewing versions. All clamps (except the viewing clamp) include tips for hard, soft and pellet shaped samples. High-pressure clamps are calibrated to deliver over 10,000 psi of pressure when used with the single reflection crystal plates.

Ability to deliver high pressure is very important for achieving spectral quality. In the example below, we demonstrate spectral differences for a porous polymer sample measured with the micrometer clamp and the high-pressure clamp. Clearly the spectrum obtained using the high-pressure clamp is required for a high quality result.

MIRacle high-pressure clamps utilize a slip-clutch mechanism to prevent excessive pressure from being applied to the crystal.

MIRacle Clamp Pressures	Max. lbs. Pressure	Crystal Diameter, mm	PSI
High-Pressure Clamps	40	1.8	10,141
		6.0	913
Micrometer Pressure Clamp	8	1.8	2,028
		6.0	183

Note: All clamps except Micrometer are high pressure



Porous Polymer Sample Measured Using High and Low-Pressure Clamp

MIRacle Sampling Options

The MIRacle can be configured with optional resistively heated crystal plates using a PIKE temperature control module. Digital and digital with PC control versions are available. The PC control module includes TempPRO software which provides a graphical user interface for temperature control and kinetic measurements.

An optional water jacket for MIRacle ATR crystal plates provides the ability to cool or elevate ATR sampling temperature via a water circulator.

TempPRO software for graphical setup and control of kinetic measurements

MIRacle with Optional Heated Crystal Plate, Flow Cell and PIKE Temperature Control Module

MIRacle ATR Summary

The MIRacle ATR accessory is a high performance FTIR sampling tool for solid, liquid, or polymer samples. Easily changeable crystal plates provide optimized spectral data for unique sample types. With options for single or three reflection crystal plates, several pressure clamp styles and heating or cooling the MIRacle is able to address a wide range of FTIR sampling applications.

Ordering Information

MIRacle Base Optics *(must select, insert spectrometer model for XX)*

Part Number	Description
025-18XX	MIRacle ATR

Notes: MIRacle Base Optics includes liquids plate, volatiles cover, purge tubes, purge kit and spectrometer base mount. Please see the FTIR instrument code sheet.

MIRacle Crystal Plates *(must select 1 or more)*

Part Number	Description
025-2100	Diamond/ZnSe Crystal Plate
025-2106	Diamond/ZnSe/HS Crystal Plate
025-2110	3 Reflection Diamond/ZnSe Crystal Plate
025-2010	ZnSe Crystal Plate
025-2030	3 Reflection ZnSe Crystal Plate
025-2050	Ge Crystal Plate
025-2070	AMTIR Crystal Plate
025-2090	Si/ZnSe Crystal Plate
025-2096	Si Crystal Plate
025-2200	Specular Reflection Plate

Notes: MIRacle Crystal Plates are pre-aligned and pinned-in-place. Changing crystal plates is easy and fast to optimize sampling results. Crystal plates are manufactured using polished stainless steel for chemical resistance. The diamond/ZnSe crystal plate is available with optional Hastelloy (HS) metal for exceptionally caustic or acidic samples.

MIRacle Sampling Options

Part Number	Description
025-5010	Water Jacket – fits all crystal plates
025-5012	Flow-through Attachment
025-4010	MIRacle Heated ZnSe Crystal Plate
025-4050	MIRacle Heated Ge Crystal Plate
025-4070	MIRacle Heated AMTIR Crystal Plate
025-4090	MIRacle Heated Si Crystal Plate (60 C Max)
025-4100	MIRacle Heated Diamond/ZnSe Crystal Plate (60 C Max)
076-1410	Digital Temperature Control Module, PC Control
076-1210	Digital Temperature Control Module

Notes: Water Jacket requires customer water circulator. Maximum crystal temperature is 130 °C, except where otherwise stated. Flow through attachment is compatible with all crystal offerings. Temperature controller selection is required for heated crystal plates. Digital temperature controller with PC control includes TempPRO software.

Specifications for Resistively Heated MIRacle Plates	
Temperature Range:	Ambient to 65 or 130 °C
Accuracy:	+/- 0.5%
Voltage:	24 VAC
Sensor Type:	3 wire Pt RTD (low drift, high stability)
Controllers	
Digital:	+/- 0.1% of set point
Digital PC:	+/- 0.1% of set point, graphical setup, up to 3 ramps, USB interface
Input Voltage:	110/220 V, switch able
Output Voltage:	10A/24 VAC

MIRacle Pressure Clamps

(must select 1 or more for solids or polymer analysis)

Part Number	Description
025-3090	Digital, High-Pressure Clamp
025-3020	High-Pressure Clamp
025-3075	Rotating, High-Pressure Clamp
025-3300	Viewer, High-Pressure Clamp
025-3050	Micrometric, Low-Pressure Clamp
025-3035	Confined Space Clamp

Notes: The High-Pressure Clamp is recommended for general applications. Pressure clamps include a flat tip, a swivel tip and a concave tip.

MIRacle Replacement Parts

Part Number	Description
025-3051	MIRacle Volatiles Cover
025-3056	Teflon Insert for Liquids Plate (set of 2)
025-3058	Teflon Insert for 3 Reflection Plate (set of 2)
025-3057	MIRacle Mounting Ring
025-3059	MIRacle Liquids Metal Plate, with Insert
025-3095	Flat tip for High-Pressure Clamps
025-3093	Swivel tip for High-Pressure Clamps
025-3092	Concave tip for High-Pressure Clamps
025-3096	Sealed Pressure Tip for High Pressure Clamp
025-3052	Flat tip for Micrometric Clamp
025-3061	Swivel tip for Micrometric Clamp
025-3054	Concave tip for Micrometric Clamp
025-3094	Pressure tip for 3 reflection crystal plates
025-3091	Digital Clamp Battery Pack

Notes: Please contact PIKE Technologies for items not described in this list.

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Specular Reflectance – *Theory and Applications*

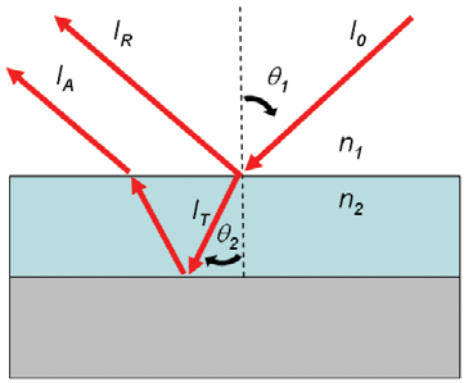
Specular reflectance sampling in FTIR represents a very important technique useful for measurement of thin films on reflective substrates, analysis of bulk materials and measurement of mono-molecular layers on a substrate material. Often the specular reflectance technique provides a means of sample analysis with no sample preparation – keeping the sample intact for other measurements.

The basics of the sampling technique involve measurement of the reflected energy from a sample surface at a given angle of incidence. The electromagnetic and physical phenomena which occur at and near the surface are dependent upon the angle of incidence of the illuminating beam, refractive index and thickness of the sample and other sample and experimental conditions. A discussion of all of the physical parameters and considerations surrounding the specular reflectance sampling technique is beyond the scope of this overview. We will present the specular reflectance sampling technique from an applications oriented perspective.

Types of specular reflectance experiments

- Reflection-Absorption of relatively thin films on reflective substrates measured at near normal angle of incidence
- Specular Reflectance measurements of relatively thick samples measured at near normal angle of incidence
- Grazing Angle Reflection-Absorption of ultra-thin films or mono-layers deposited on surfaces measured at high angle of incidence

In the case of a relatively thin film on a reflective substrate, the specular reflectance experiment may be thought of as similar to a "double-pass transmission" measurement and can be represented as shown in the following illustration;

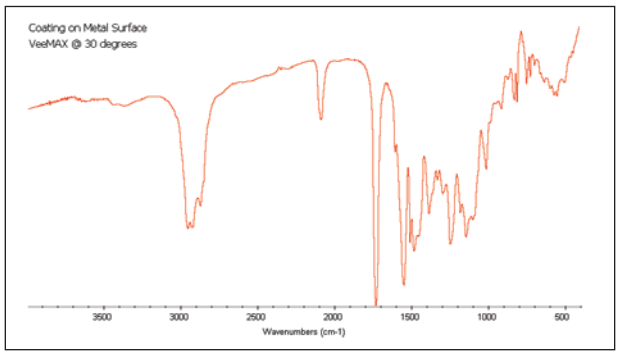


Beam path for Reflection-Absorption of a relatively thin film measured by Specular Reflectance

The incident FTIR beam represented by I_0 illuminates the thin film of a given refractive index, n_2 and at an angle of incidence, θ_1. Some of the incident beam is reflected from the sample surface, represented by I_R at the incident angle, θ_1 and is also known as the specular component. Some of the incident beam is transmitted into the sample represented by I_T at an angle of θ_2 – calculated from Snell's Law.

$$n_1 \sin\theta_1 = n_2 \sin\theta_2$$

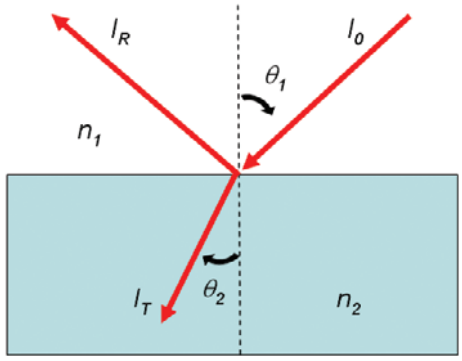
At the reflective substrate, the beam reflects back to the surface of the thin film. When the beam exits the thin film it has geometrically passed through the film twice and is now represented as I_A. Infrared energy is absorbed at characteristic wavelengths as this beam passes through the thin film and its spectrum is recorded. The specular reflectance spectra produced from relatively thin films on reflective substrates measured at near-normal angle of incidence are typically of high quality and very similar to spectra obtained from a transmission measurement. This result is expected as the intensity of I_A is high relative to the specular component, I_R.



Spectrum of thin film coating on a metal surface measured at 30 degrees angle of incidence using the VeeMAX II specular reflectance accessory

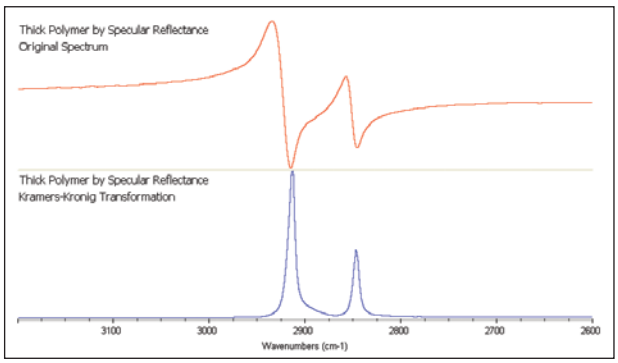
For relatively thick samples, the specular reflectance experiment produces results which require additional considerations as the specular component of the total reflected radiation is relatively high.

Again, the incident FTIR beam represented by I_0 illuminates the sample of a given refractive index, n_2 and at an angle of incidence, θ_1. Some of the incident beam is reflected from the sample surface, represented by I_R at the incident angle, θ_1. Some of the incident beam is transmitted into the sample represented by I_T at an angle of θ_2. As predicted by Fresnel equations, the percent of reflected vs. transmitted light increases with higher angles of incidence of the illuminating beam. Furthermore, the refractive index of the sample, surface roughness and sample absorption coefficient at a given wavelength all contribute to the intensity of the reflected beam.



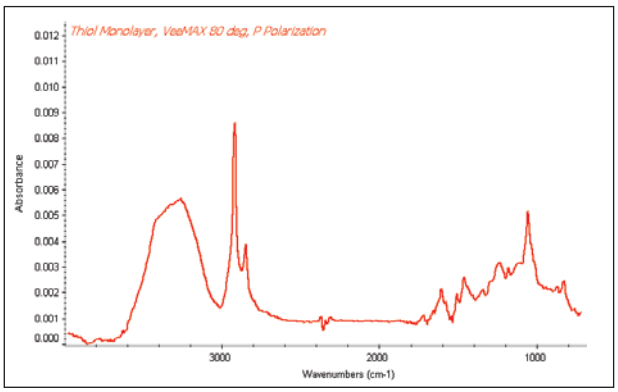
Beam path for a relatively thick sample measured by Specular Reflection

At wavelengths where the sample exhibits a strong IR absorption, the reflectivity of the sample increases. The superposition of the extinction coefficient spectrum with the refractive index dispersion results in a spectrum with derivative shaped bands. This specular reflection spectrum can be transformed using a Kramers-Kronig conversion to a transmission-like spectrum as shown in the example below.



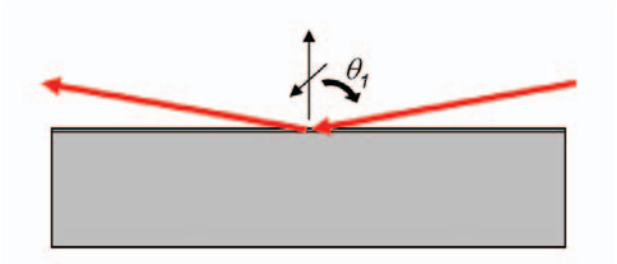
Spectrum (upper – original) of a relatively thick polymer sample measured at 30 degrees angle of incidence using the VeeMAX II. The lower spectrum has been transformed using the Kramers-Kronig software algorithm and is very similar to a transmission spectrum of the polymer – polyethylene.

Because of the orientation of the electro-magnetic field at the surface for grazing angle measurements, the use of an IR polarizer greatly improves the sampling result. By collecting the spectrum at grazing angle of incidence with P-polarization, we only examine the enhanced portion of the electromagnetic field at the sample surface, thereby producing a stronger absorbance spectrum.



Grazing angle specular reflection analysis of a thiol mono-molecular layer deposited on a gold surfaced mirror using the PIKE VeeMAX II at 80 degrees and P-polarization. The FTIR was equipped with an MCT detector.

Our third application of specular reflectance is the measurement of relatively thin films and mono-molecular layers at grazing angle of incidence. At high angles of incidence, between 60 and 85 degrees, the electromagnetic field in the plane of the incident and reflected radiation is greatly increased relative to a near normal angle of incidence. The perpendicular component of the electromagnetic field of the reflecting radiation is not enhanced.



Grazing angle specular reflection analysis produces a strong electromagnetic field oriented in the plane of the incident and reflected radiation

Specular reflectance is a valuable FTIR sampling technique for the analysis of thin films on reflective substrates, for the analysis of relatively thick films on reflective materials and for analysis of bulk materials where no sample preparation is preferred. PIKE Technologies offers a complete line of specular reflectance accessories and options to do these analysis and perform these experiments.

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