

Introduction to Attenuated Total Reflection (ATR) Spectroscopy

Theory

Under certain conditions, radiant energy incident on an internal surface of a high refractive index transparent material is totally reflected. When an infrared absorbing material is in optical contact with a totally internally reflecting surface, the intensity of the internally reflected radiation is diminished for those wavelengths or energies where the material absorbs energy. Since an internal reflecting surface is essentially a perfect mirror, the attenuation of this reflected intensity by a material on its surface

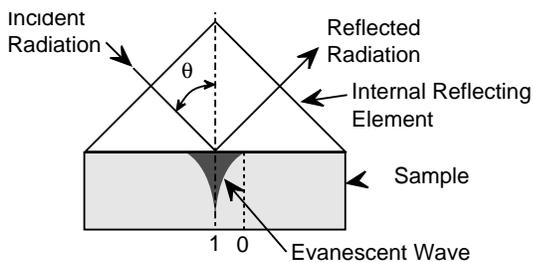


Figure 1

provides a means of producing an absorption spectrum of the material. Such spectra are called internal reflection spectra or attenuated total reflection (ATR) spectra. ATR is the most commonly accepted descriptor for this spectral collection technique. It is convenient to regard the process as internal reflection and the data as ATR spectra. The high index of refraction material used to create internal reflection is called an internal reflection element (IRE) or an ATR crystal. Both terms are common. Figure 1 illustrates the general features of an internal reflection configuration and labeling of various components.

The attenuation of the internally reflected radiation results from the penetration of the electro-magnetic radiation field into the matter in contact with the reflection surface. This field was described by N.J. Harrick (1965) as an evanescent wave. It is the interaction of this field with the matter in contact with the IRE interface that results in attenuation of the internal reflection. One of the most useful characteristics of this field is that its strength decreases rapidly with increasing depth of penetration into the material. In general the depth of penetration is such that ATR spectra can be easily collected on thick and, or optically dense samples.

Factors Affecting ATR Spectral Analysis

The factors which affect the results obtained in an ATR experiment are the:

- Wavelength of Infrared Radiation
- Refractive Index of the IRE and sample
- Depth of Penetration
- Effective Pathlength
- Angle of Incidence
- Efficiency of Sample Contact
- ATR Crystal Material

Wavelength of Infrared Radiation

The penetration depth of the infrared energy into the sample is wavelength dependent. As the wavelength of the infrared radiation increases, the depth of penetration increases. It is often convenient to discuss this in terms of wavenumbers: the depth of penetration decreases when wavenumber increases. This causes the relative band intensities in the ATR spectrum to decrease with increasing wavenumbers when compared to a transmission spectrum of the same sample. This phenomenon can be mathematically corrected by most commercial FT-IR software packages.

Refractive Index

The refractive index of the IRE has two effects on the ATR spectrum obtained: 1- By increasing the refractive index of the IRE material, the

critical angle θ_c is decreased. The critical angle is a function of the refractive indices of the sample and ATR crystal and is defined as:

$$\theta_c = \sin^{-1}(n_2/n_1)$$

where n_1 is the refractive index of the ATR crystal and n_2 is the refractive index of the sample. 2- The refractive index also affects the depth of penetration of the evanescent wave into the sample. By increasing the refractive index of the IRE, the depth of penetration will decrease (i.e. changing from ZnSe to Ge). This will decrease the effective pathlength and therefore decrease the absorbance of the spectrum. High index ATR crystals are needed when analyzing high index materials.

Depth of Penetration

Control of depth of penetration is obtained by altering the angle of incidence of the incoming IR beam with respect to the crystal or changing the refractive index of the crystal.

A useful relationship in ATR spectroscopy which can be used as a qualitative measure of the depth which the evanescent wave extends into the sample is defined as the depth of penetration, dp . The depth of penetration is the distance from the crystal-sample interface where the intensity of the evanescent wave decays to $1/e$ (approximately 37%) of its original value. It is calculated by:

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

where λ is the wavelength of infrared radiation, n_2 is the ratio of the refractive index of the sample to the refractive index of ATR crystal, and θ is the angle of incidence (see following page). If the calculation takes into consideration polarization, the reflected field amplitudes of the crystal are different for equal incident amplitudes of perpendicular and parallel polarization. The effective penetration (EP) are mathematically different for the two polarizations. The relative effective penetration (EP) for an isotropic medium for perpendicular and parallel polarizations are:

$$EP_{\perp} = \frac{\lambda n_2 \cos\theta}{\pi(1 - n_2^2)(\sin^2\theta - n_2^2)^{1/2}}$$

and

$$EP_{\parallel} = \frac{\lambda n_2 \cos\theta(2\sin^2\theta - n_2^2)}{\pi(1 - n_2^2)\{(1 + n_2^2)\sin^2\theta - n_2^2\}(\sin^2\theta - n_2^2)^{1/2}}$$

where λ is the wavelength of infrared radiation, n_2 is the ratio of the refractive indices of the sample to the IRE and θ is the angle of incidence. The values in the table (see following page) are the average of the parallel and perpendicular polarizations, or $EP = (EP_{\perp} + EP_{\parallel}) / 2$.

The depth of penetration (as calculated above) is useful for comparing the effects of the IRE refractive index, the angle of incidence and the state of polarization. However, the experimental sampling depth is 2 to 3 times the theoretical depth of penetration.

Effective Pathlength

The Effective Pathlength (EPL) can be used as an approximate comparison between the expected absorbance of an ATR spectrum and a transmission spectrum. In a spectrum obtained by transmission, the pathlength is the thickness of the sample which is directly related to the absorbance. In ATR, the effective pathlength is calculated as:

$EPL = \text{Effective Penetration} \times \text{Number of Reflections (N)}$, where:
 $N = l/t \cot\theta$; l = length of crystal, t = thickness of crystal and θ = angle of incidence

For horizontal ATRs divide N by 2. The EPL is directly related to the absorbance in that, an increase in either the effective penetration or the number of reflections will increase the absorbance of the spectrum.

ATR Calculations (NOTE: $n_2 = 1.5 @ 1000 \text{ cm}^{-1}$)

| θ | # of reflections (HATR) | ZnSe ($n_1 = 2.4$) | | | Ge ($n_1 = 4$) | | | AMTIR ($n_1 = 2.5$) | | |
|------------|-------------------------|----------------------|-------|----------------------|------------------|-------|----------------------|-----------------------|-------|----------------------|
| | | dp | EP | EPL(μm) | dp | EP | EPL(μm) | dp | EP | EPL(μm) |
| 30 | 21 | NA | NA | NA | 1.2 | 0.842 | 17.68 | NA | NA | NA |
| 40 | 14 | 4.4 | 3.26 | 45.64 | 0.763 | 0.303 | 4.24 | 2.76 | 1.845 | 38.75 |
| 45 | 12 | 2.0 | 1.01 | 12.12 | 0.664 | 0.216 | 2.59 | 1.70 | 0.807 | 9.68 |
| 50 | 10 | 1.5 | 0.582 | 5.82 | 0.596 | 0.162 | 1.62 | 1.34 | 0.493 | 4.93 |
| 55 | 8 | 1.25 | 0.389 | 3.11 | 0.547 | 0.124 | .992 | 1.14 | 0.339 | 2.71 |
| 60 | 7 | 1.11 | 0.277 | 1.94 | 0.510 | 0.096 | .672 | 1.02 | 0.245 | 1.72 |
| θ_c | | 38.68 | | | 22.02 | | | 36.87 | | |

Angle of Incidence

Changes in the angle of incidence of the infrared radiation have three effects on the ATR spectrum of a sample. The first is that an angle of incidence must be chosen to exceed the critical angle in order to have internal reflection and produce an ATR spectrum.

In multiple internal reflection, the angle of incidence also has an effect on the number of reflections in the ATR crystal. This affects the infrared absorbance. As the angle of incidence increases, the number of reflections decreases and the absorbance decreases.

Changing the angle of incidence also changes the depth of penetration. If the angle of incidence is increased, the depth of penetration will be decreased and the absorbance will be decreased.

The condition which must exist to obtain total internal reflection is that the angle of the incident radiation, θ , must exceed the critical angle, θ_c . High refractive index materials are chosen for the ATR crystal to minimize the critical angle.

Efficiency of Sample Contact

Another factor which affects the quality of an ATR spectrum is the efficiency of sample contact. Because the evanescent wave decays very rapidly with distance from the surface, it is important to have the sample in intimate optical contact with the crystal. This is easily achieved with liquids since they wet the surface of the ATR crystal. For solids, it is important to use a device which presses the sample against the IRE.

IRE Crystal Material

The IRE material defines its refractive index, the infrared transmission range, and the chemical properties of the crystal. A crystal material must have a higher index of refraction than the sample to allow internal reflection. Materials with a refractive index greater than 2.2 are normally chosen as ATR crystals.

An ATR crystal material should also be chosen by the sample's useful pH range. For ZnSe, the most common IRE, a pH between 5 and 9 is required ($n = 2.4$). AMTIR and Ge are recommended for use with acids. Either ZnS or Ge are the recommended choices for use with bases. However, Ge has high reflection losses and lower throughput than ZnS, while ZnS has a limited spectral range. See page 11-4 for additional crystal material information.

Introduction to Diffuse Reflection Spectroscopy

Using Diffuse Reflection Spectroscopy, samples can be analyzed either directly or as dispersions in non-absorbing matrices - e.g. alkali halides (such as KBr) for qualitative analysis. Even intractable samples, such as cured epoxy resins, can be analyzed with the aid of the Si-Carb™ Sampler. Diffuse Reflection eliminates the need for heavy duty presses or the oily mess of a mull.

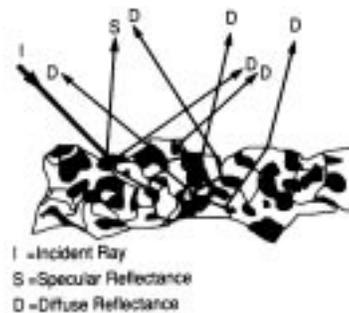
The high throughput and signal-to-noise ratios of FT-IR spectrometers, in combination with on-axis diffuse reflection accessories, have made diffuse reflection a powerful infrared technique. Currently DRIFTS (Diffuse Reflection Infrared Fourier Transform Spectroscopy) offers a number of advantages as an analytical technique, including:

- Minimal or no sample preparation.
- Very high sensitivity (down to low ppm levels).
- Ability to analyze most non-reflective materials, including highly opaque or weakly absorbing materials.
- Ability to analyze irregular surfaces or coatings, such as polymer coatings.
- Suitability for very large, intractable samples through the use of specialized sampling devices.

Theory

When infrared radiation is directed onto the surface of a solid sample, two types of reflected-energy can occur. One is specular reflection and the other is diffuse reflection. The specular component is the radiation which reflects directly off the sample surface (it is the energy which is not absorbed by the sample). Diffuse reflectance is the radiation which penetrates into the sample and then emerges (see Figure 2). A diffuse reflection accessory is designed so the diffusely reflected energy is optimized and the specular component is minimized. The optics collect the scattered radiation and direct it to the infrared detector.

The sample is usually ground and mixed with a material such as KBr, that acts as a non-absorbing matrix. By diluting the sample in a non-absorbing matrix, the proportion of the infrared beam that is diffusely reflected by the sample is increased. Typically for organic samples the analyte is mixed in a 1 to 9 ratio in KBr (10% by weight), and for inorganics, a 1 to 20 ratio in KBr (5% by weight).

**Figure 2**

Quantitative Measurements – The Kubelka-Munk Equation

A theory of diffuse reflection at scattering surfaces is the Kubelka-Munk theory, developed in 1931. The Kubelka-Munk model relates sample concentration to the intensity of the measured infrared spectrum. The Kubelka-Munk equation is generally expressed as:

$$f(R) = \frac{(1 - R)^2}{2R} = \frac{k}{s}$$

where R is the absolute reflectance of the layer, k is the molar absorption coefficient and s is the scattering coefficient.

The Kubelka-Munk theory predicts a linear relationship between spectral intensity and sample concentration under conditions of a constant scattering coefficient and infinite sample dilution in a non-absorbing matrix. Hence, the relationship can only be applied to highly diluted samples in a non-absorbing matrix such as KBr. In addition, the scattering coefficient is a function of particle size. The samples must be ground to a uniform, fine size if quantitatively valid measurements are desired. Finally, the equation only applies to an "infinitely thick" sample layer, which in infrared spectroscopy occurs at a sample thickness of approximately 3 mm. These restrictions reduce the number of spectra presentable in Kubelka-Munk units, but do not restrict "non-ideal" samples from quantitative diffuse reflection analysis. Typically, quantitative diffuse reflection measurements are presented in $\log 1/R$ units, analogous to absorbance $\log 1/T$ units for transmission measurements.

Factors Affecting Spectral Data

Several factors exert a significant influence over bandshape and relative/absolute intensity. These include:

- Refractive index of the sample and matrix
- Particle size
- Sample homogeneity and loading
- Concentration

Refractive Index of the Sample and Matrix

Refractive index effects result in specular reflection contributions. With organic samples, spectra display changes in bandshape and relative peak intensities which result in nonlinearity of the relationship between band intensity and sample concentration. For inorganic samples, strong specular reflection contributions can result in complete band inversions (restrahlen bands). This effect can be minimized by dilution of the sample in a non-absorbing matrix. In addition, the COLLECTOR™ employs the BLOCKER™,

which is a knife edge divider which prevents surface reflected radiation from reaching the detector. However, because diffuse and specular components are randomly directed, the BLOCKER is not able to completely eliminate all of the specular contributions.

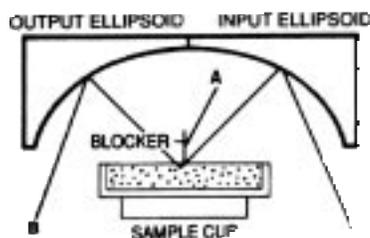


Figure 3: The BLOCKER

Particle Size

Particle size is a major consideration when performing diffuse reflection measurements. The bandwidths decrease and relative intensities are dramatically altered as particle size decreases. To acquire a high quality diffuse reflection spectrum, it is necessary to uniformly grind the sample to less than 50 μm in size, and dilute it in a fine, non-absorbing matrix.

Sample Homogeneity

The Kubelka-Munk model for diffuse reflectance is derived for a homogeneous sample of infinite depth. To avoid peak intensity variations, it is necessary to distribute the analyte as uniformly as possible within the non-absorbing background matrix. The desired way to load a sample cup is to loosely pack it, and have a level surface.

Concentration

One important advantage of diffuse reflection spectroscopy is its extremely broad sample concentration range. While it is theoretically possible to acquire usable diffuse reflection spectra on samples ranging from highly dilute to neat, practical considerations often limit the analysis range.

With high concentration samples, especially those with a high refractive index, you can expect a dramatic increase in the specular contribution to the spectral data. As a result, some sample data may be uninterpretable without adequate sample dilution. Even when samples can be measured satisfactorily at high concentration, it is advisable to grind the sample to a very uniform, very fine particle size to minimize both specular reflection and sample scattering effects which adversely affect quantitative precision.

Introduction to External Reflection Spectroscopy

External reflection techniques provide a non-destructive method for measuring surfaces and coatings without sample preparation. Typical samples include surface-treated metals, resin and polymer coatings, paints, semiconductors and many more.

True specular reflection is a mirror-like reflection from the surface of a sample. The infrared radiation is directed onto the surface of the sample at an angle of incidence, I . For specular reflection, the angle of the reflection, R , is equal to the angle of incidence, I (Figure 4). The amount of radiation reflected depends on the angle of incidence, the index of refraction of the sample, surface roughness and the absorption properties of the sample.

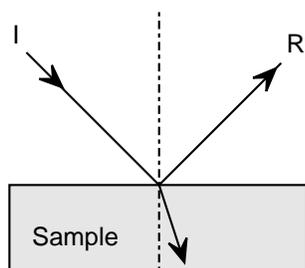


Figure 4

Depending on the type of sample, certain external reflection techniques will have advantages over others. For example, smooth, highly reflective surfaces are ideal candidates for specular reflection. Thick samples on reflective surfaces are best analyzed by near-normal Reflection-Absorption (Figure 5). For submicron films on reflective surfaces, grazing angle Reflection-Absorption is the best technique.

The angle of incidence is selected depending on the thickness of the coating which is being studied. For very thin coatings in the nanometer thickness range, an 80° angle of incidence would be chosen. Reflection measurements at this angle of incidence are often referred to as grazing angle measurements. For more routine samples which would have coatings in the micrometer range, a 30° angle of incidence is normally chosen.

Specular Reflection

The specular reflection technique collects only that radiation reflecting off the sample's front surface. Since specular reflection is often measured at or near normal incidence, the reflected energy is small - only 5-10% for most organic materials (for those spectral regions where the material is non-absorbing). However, in regions of strong absorption, reflected intensity is much greater. The reflected radiation intensity data is usually very different from transmission spectra, since derivative shaped bands result from the superposition of the normal extinction coefficient spectrum with the refractive index dispersion.

The utility of the specular reflection technique has increased because of the availability of fast Kramers-Kronig transform programs for data processing. Now, distorted appearing specular reflection data can be transformed into transmission-like spectra in seconds.

Strongly absorbing materials, such as silicates, strongly reflect radiation over a specific energy range, producing unique spectral features called *restrahlen* bands. Many minerals and glasses are characterized by these spectra.

Near-Normal Reflection-Absorption

In one of the most common and straightforward external reflection techniques, the IR beam travels through the sample, reflects off a reflective surface and passes a second time through the sample at an angle between 10 and 60 degrees. By placing the sample on a reflective surface, the energy obtained through the sample and off the metal is higher than that obtained from specular reflection off the sample's surface. When this condition is met, the data is completely analogous to transmission data, since the beam is simply doing a double pass transmission through the sample film. The reflection-absorption pathlength is greater than the transmission pathlength for a given thickness of film due to this double pass of the beam through the sample. The effective sample pathlength is also increased, to a lesser degree, by the beam passing through the sample at an angle. Samples analyzed by near-normal reflection-absorption are typically in the $0.5 - 20$ micron thickness range.

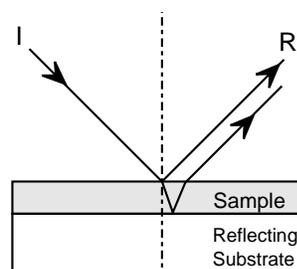


Figure 5

Grazing Angle Reflection-Absorption

Grazing angle reflection-absorption spectral measurements are more sensitive than near-normal incidence measurements of very thin films on reflective surfaces. When radiation is incident on a surface at angles between 60 to 85° , the electro-magnetic field in the plane containing the incident and reflected radiation is greatly increased. This large electro-magnetic field is oriented normal to the reflecting surface. At normal incidence, the electro-magnetic field strength at the reflecting surface approaches zero, but increases to full amplitude one quarter wavelength from the surface. Therefore, for films less than one quarter of a wavelength thick, grazing angle measurements are preferred over near-normal incidence measurements.

Not only is the sensitivity increased at the grazing angle, but the orientation of the molecules on surfaces can be determined. There are two vectors present at the surface: a p -polarized component, which is in the same plane as the incident and reflecting radiation, and an s -polarized component, which is perpendicular to the plane. The distinction between these two states of polarization is important in grazing angle reflection-absorption infrared analysis. Only the p -polarized component has an enhanced electro-magnetic field at the surface. The s -polarized component's field approaches zero, just as in near normal incidence. For molecules on a surface, only those bonds with dipole components normal to the surface can absorb infrared radiation. Therefore, grazing angle measurements are also useful for molecular orientation studies. This factor, along with the increased sensitivity, make grazing angle reflection-absorption spectroscopy a very important technique.