



Introduction to Attenuated Total Internal Reflectance(ATR)

INTRODUCTION

Attenuated Total Internal Reflectance (ATR) Spectroscopy is a versatile and powerful technique for infrared sampling. Minimal or no sample preparation is usually required for rapid analysis. ATR is ideal for those materials which are strong absorbers. In addition, ATR is a useful technique for providing information about the surface properties or conditions of a material.

THEORY

The phenomenon of internal reflection was first reported in infrared spectroscopy in 1959. It was observed that if certain conditions were met, infrared radiation entering a prism made of a high refractive index infrared transmitting material (ATR crystal) will be totally internally reflected (Figure 1). This internal reflectance creates an evanescent wave which extends beyond the surface of the crystal into the sample held in contact with the crystal. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will be attenuated.

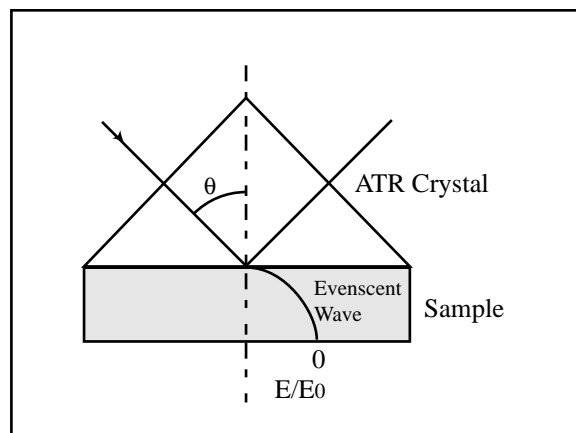
The condition which must exist to obtain total internal reflectance is that the angle of the incident radiation, θ , must exceed the critical angle, θ_c . The critical angle is a function of the refractive indices of the sample and ATR crystal and is defined as:

$$\theta_c = \sin^{-1} \frac{n_2}{n_1}$$

where n_1 is the refractive index of the ATR crystal and n_2 is the refractive index of the sample. High refractive index materials are chosen for the ATR crystal to minimize the critical angle.

A property of the evanescent wave which makes ATR a powerful technique is that the intensity of the wave decays exponentially with distance from the surface of the ATR crystal. The distance, which is on the

order of microns, makes ATR generally insensitive to sample thickness, allowing for the analysis of thick or strongly absorbing samples.



DEPTH OF PENETRATION

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, d_p . The depth of penetration is defined as 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:

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

where λ is the wavelength of infrared radiation, n_1 is the refractive index of the ATR crystal, θ is the angle of incidence, and n_2 is the ratio of the refractive indices of the sample and the ATR crystal.

EFFECTIVE PATHLENGTH

A second useful relationship is known as the Effective

Pathlength (EPL). The EPL can be used as an approximate comparison between the expected absorbance intensity 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 intensity. In ATR the Effective Pathlength can be calculated as:

$$\text{EPL} = \text{Penetration Depth} \times \text{Number of Reflections.}$$

The EPL is also directly related to the absorbance intensity. An increase in either the depth of penetration or in the number of reflections will increase the absorbance intensity of the spectrum.

Factors Affecting the ATR Spectrum

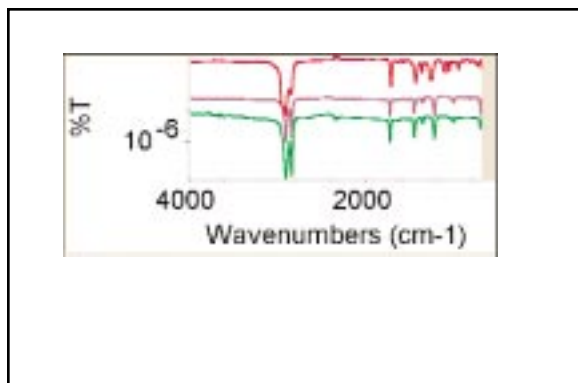
The factors which effect the results obtained in an ATR experiment are the:

- o Wavelength of Infrared Radiation
- o Refractive Index of the ATR crystal
- o Angle of Incidence
- o Efficiency of Sample Contact
- o Area of Sample Contact
- o 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 also increases. It is often convenient to discuss this in terms of wavenumbers: the depth of penetration decreases when wavenumber increases. This leads to the relative band intensities in the ATR spectrum to decrease with increasing wavenumbers when compared to a transmission spectrum of the same sample (Figure 2).

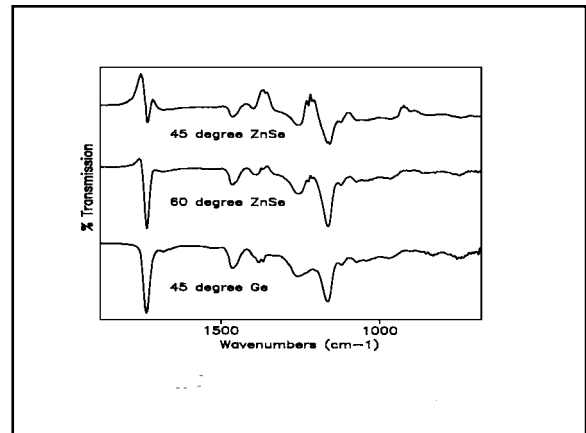
Since band positions and shapes are nearly identical for the ATR and the transmission spectrum, many spectrometers have an "ATR Correction" program which makes the ATR spectrum appear more like a transmission spectrum.



REFRACTIVE INDEX

The refractive index of the ATR crystal has two effects on the ATR spectrum obtained. The first is that by increasing the refractive index of the crystal material, the critical angle is decreased. This is important when working with samples which have a high index of refraction. Distortions in the infrared spectrum of the sample will be observed if the angle of incidence does not greatly exceed the critical angle (Figure 3). Figure 3

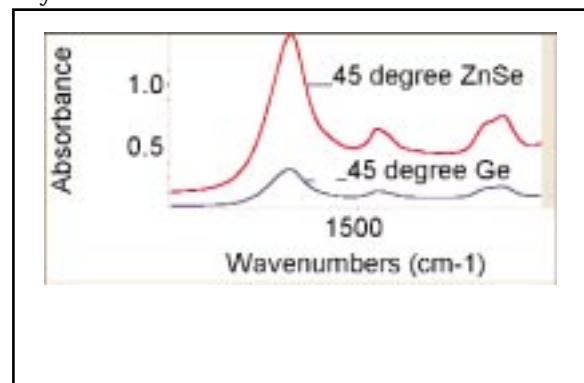
The refractive index also affects the depth of penetra-



tion of the evanescent wave into the sample. By increasing the refractive index of the ATR crystal, the depth of penetration will decrease. This will decrease the Effective Pathlength and therefore decrease the absorbance intensity of the spectrum (Figure 4).

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 obtain an ATR spectrum. An example of this is shown below for a ZnSe crystal with a refractive index of 2.4 and a Ge crystal which has a refractive index of 4.0 for a



sample of refractive index of 1.5.

For ZnSe:

For Ge:

If an angle of incidence of less than 38.7° was chosen for the ZnSe crystal, internal reflection would not occur and a spectrum of the material would not be obtained. An angle of incidence should be chosen to

$$\theta_c = \sin^{-1} \frac{1.5}{2} = 38.7^\circ$$

greatly exceed the critical angle such as a 45° crystal

$$\theta_c = \sin^{-1} \frac{1.5}{4} = 22.0^\circ$$

in this example.

The angle of incidence also has an effect on the number of reflections in the ATR crystal which affects the infrared absorbance intensity of the spectrum. As the angle of incidence increases, the number of reflections decreases and the absorbance intensity 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 intensity will be decreased.

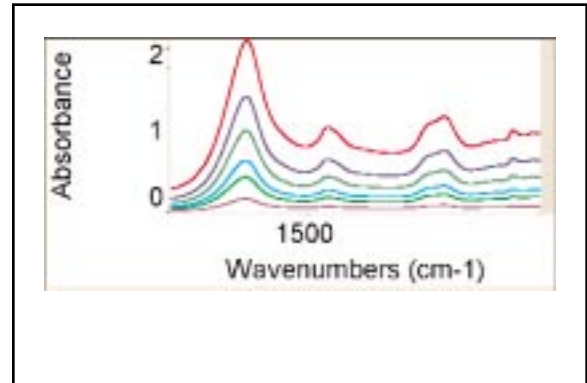
The effect of the changes in the angle on the Effective Pathlength which is a product of the number of reflections and the depth of penetration is illustrated in Figure 5. Four ZnSe Contact Sampler crystals were chosen at different angles of incidence. As the angle of incidence is increased, the Effective Pathlength is decreased and the absorbance intensity is decreased.

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 contact with the crystal. This is easily achieved with most liquids since they wet the surface of the ATR crystal. For solids, it is important to use a pressure device which presses the sample against the crystal (Figure 6). A plot of the absorbance intensity versus pressure shows that by increasing the pressure of some samples, the contact efficiency is increased (Figure 7). For very hard materials, care must be taken when increasing the pressure on the crystal so as not to damage the crystal.

AREA OF SAMPLE CONTACT

The Area of Sample Contact directly affects the



intensity of the absorbance spectrum. If the entire

Figure 5

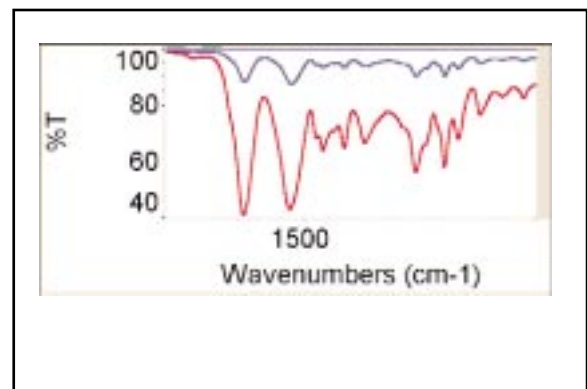


Figure 6

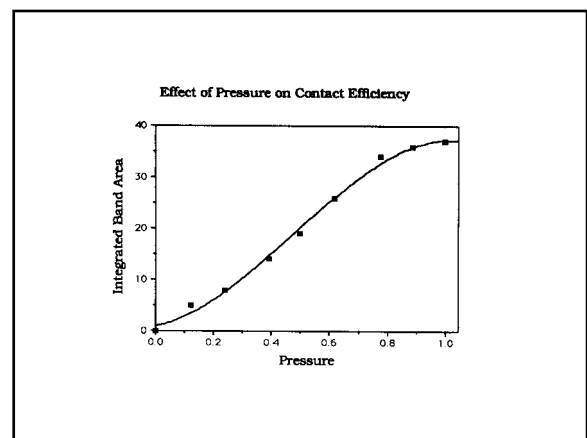


Figure 7

crystal surface is not covered, the intensity of the absorbance spectrum will decrease (Figure 8). To ensure maximum reproducibility in a series of measurements, the entire crystal surface should be covered by the sample.

ATR CRYSTAL MATERIAL

The material from which the ATR crystal is made from will affect the refractive index, the infrared transmission range, as well as the chemical properties of the crystal. A crystal material must have a high index of refraction to allow internal reflectance. Materials with a refractive index greater than 2.2 are normally chosen as ATR crystals.

The material which is most commonly used for ATR spectroscopy is ZnSe. ZnSe has a refractive index of 2.4 making it suitable for most organic materials and it has a transmission range from 20,000 to 650 cm^{-1} . This material is insoluble in water but should not be used in acidic or strong alkaline solutions.

Listed in Table 1 are some other common materials used for ATR spectroscopy with their transmission ranges and their chemical properties. Special care

must be used in selecting a material if working with samples which are either acidic or alkaline.

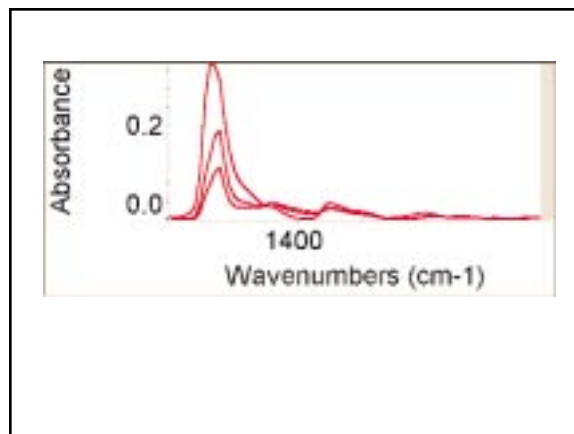


Figure 8

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Spectra-Tech Inc., 2 Research Drive, Shelton, CT 06484-0869
Tel: 203-926-8998, Toll-free 800-243-9186, FAX: 203-926-8909
website: www.spectra-tech.com, e-mail: info@spectra-tech.com

S T Japan, 1-14-10 Kakigara-cho, Nihonbashi, Chuo-ku
Tokyo, 103 Japan, Tel: (033) (666) 2561, FAX: (033) (666) 2658
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