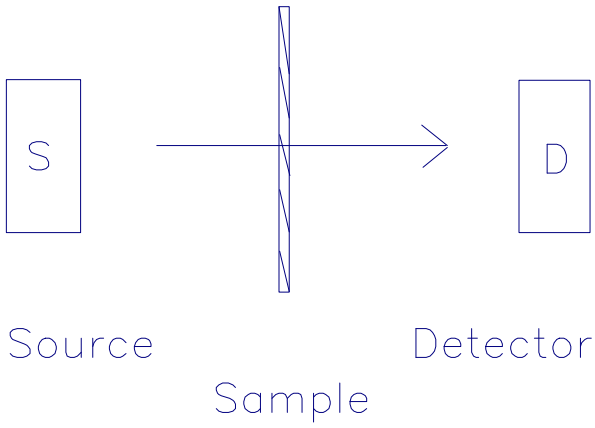
TN-101

FTIR SAMPLING TECHNIQUES

by Hue Phan

A choice on sampling technique exists for all types of sample. The chosen technique depends of the application and the sample states. The common techniques are described in detail as follows:

Transmission



Liquid Samples:

Neat sample: A drop of sample is pressed between two halide salt crystals. A clean crystal window can be used as reference background.

Diluted solution: Sample is diluted in a suitable solvent. A drop of the prepared solution is then pressed between two crystal windows. A reference spectrum of the diluting solvent may be obtained and subtracted from the solution spectrum. Carbon tetrachloride and carbon disulfide solvents are commonly used for dilution.

Liquid cell: Liquid cells are available with either a fixed or an adjustable pathlength. For quantitative analysis, this is one of the most economic techniques for liquid samples which requires a known pathlength, however, it is often difficult to clean out the cell and also leaking problem might occur. Cells should be filled carefully to avoid air bubbles. Samples can be measured as either neat or diluted solution. A variety of window materials are available upon request.

Solid Samples:

Neat sample: Semi-solid of low melting materials may be heated and spreaded across the crystal window in a thin film with a spatula.

Cast films: Sample is dissolved in a suitable solvent. A drop of the prepared solution is then placed on the crystal window to allow the solvent to evaporate. A thin film of sample is left on the crystal for infrared measurement.

Pressed films: Plastic materials can be pressed into thin films by using heated platens if decomposition, oxidation and degradation is not a problem.

KBr pellets: Sample is ground thoroughly with KBr at approximately 1% to 3% by weight and pressed into a pellet with a thickness of about 1mm. A hand presser or a KBr die with a variety of sizes, ranging from 0.5mm to 13mm, are available to make pellets. Open beam air background is typically used for this technique.

Mull: Sample is ground and mixed with Nujol or Fluorolube. The mixture is then spreaded on the crystal window for measurement. Absorption bands of the oil will obscure some of the sample's features. Nujol has absorption bands at short wavelengths and Flourolube at longer wavelengths. Running the sample in both oils, separately, of course, will yield a complete spectral range of the sample. The spectrum of the pure sample may also be obtained by subtracting out the mulling material.

For a reference background, a clean crystal window or a pure KBr pellet or an open beam air may be used appropriately for the above techniques.

Gas Samples:

Short path cell: A 5cm or 10cm cell is usually used for high concentration gases. It is ideal for pure gases and mixtures.

Long path cell: A longer pathlength gas cell, available from 10m to 100m, is required for low concentration gases. Some long path cells come with adjustable pathlength. Standard window material for gas cell is KBr, other materials are available upon request.

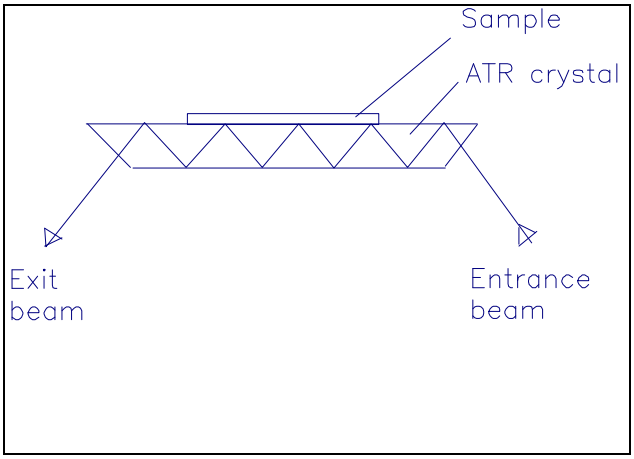
OTHER METHODS USING SAMPLING ACCESSORIES

Attenuated Total Reflectance (ATR):

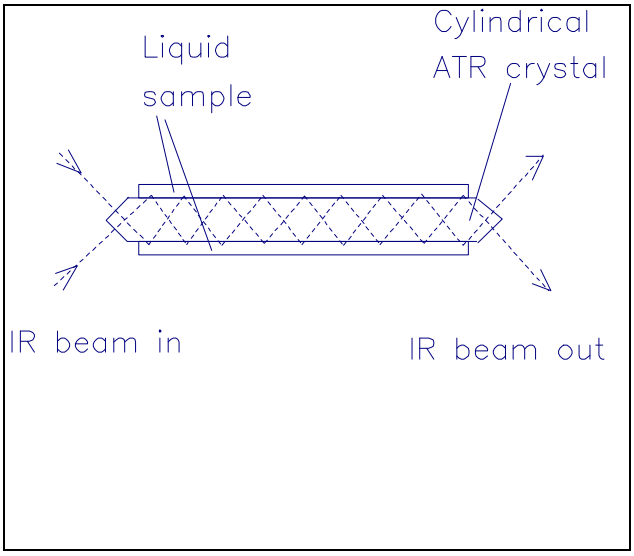
ATR is a technique for looking at the surfaces of materials. Liquids, semi-solids and pliable solids such as rubber and plastics may be easily analyzed using an ATR spectroscopy.

This method works well with samples that are too opaque or too thick for standard transmission methods. The sample is placed in contact with a crystal of high refractive index where total internal reflection occurs along the crystal-sample interface. The IR beam entering the crystal is reflected within the crystal, the number of reflections depending upon the crystal length, its thickness and the
interface angle. At each reflection, the light beam penetrates the sample to a depth of a few microns and is absorbed at the characteristic absorption frequencies. Zinc Selenide (ZnSe) crystal is most commonly used for ATR accessory.

The IR beam enters and leaves the multiple internal reflection ATR plate at 45 degrees angle. This horizontal ATR is ideal for large or odd shaped samples as well as liquids. It features a large sampling surface for easy sample mounting.

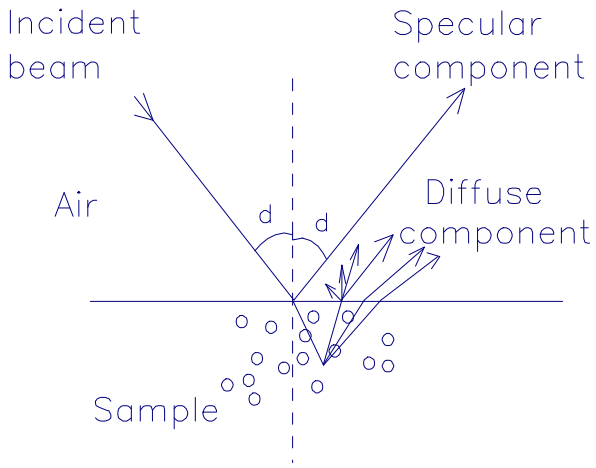


For liquids, a suitable ATR cell is designed to hold the liquids in contact with the reflecting surface. The ATR crystal is a rod with 45 degrees angle cone shaped ends. A cylindrical ATR in an open boat type cell or a flow through cell is commonly available for both stationary of flowing liquids. The volume required to fill up the cell is from 40ul to 2ml.



Another common ATR accessory is the variable angle ATR. By varying the angle of incidence, the depth of infrared penetration can be adjusted. This device is designed to analyze films, adhesives and especially samples with multiple layers of coating. The ATR crystal is mounted vertically which limits the capability of measuring liquid samples.

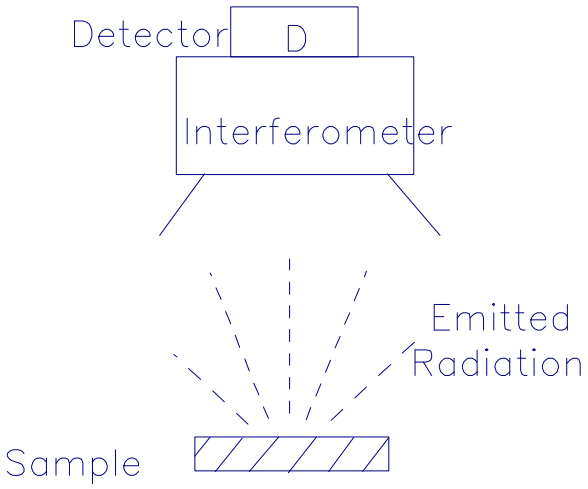
Diffuse and Specular Reflectance



Diffuse Reflectance: This technique can be applied to a wide variety of opaque or powdered samples and highly scattering samples. For powdered sample, a very small amount of sample is required for preparation which makes the technique also useful for microsampling analysis. The sample is finely ground with KBr powder at about 0.5% to 1% concentration by weight. The sample is placed in a small sample cup, sizing from 2mm and 10mm in diameter. The 10mm diameter cup requires approximately 500mg of powder to fill the cup while the smaller cup requires only 7mg to 10mg of powder. Pure KBr powder is used for reference background. Band intensities of the diffuse reflectance spectra are proportional to the square root of the concentration. Thus, the diffuse reflectance spectra must be converted into Kubelka-Munk format in order to make band intensities linear with concentration.

Specular Reflectance: This technique is most often used to analyze thin coating on metal surface or sample with a very smooth surface. When reflection takes place at the metal substrate, the specular reflectance spectrum is actually the reflection-absorption spectrum which is closely resemble the transmission spectrum. However, when the reflection takes place at the smooth surface of the sample, the spectrum recorded will exhibit absorption bands whose shapes resemble first derivatives. In this case the spectrum may be converted to transmission-like spectrum by using Kramers-Kronig software. Any highly reflective surface may be used as reference background for this technique.

Emission



Infrared emission technique is primarily useful for remote sensing and high temperature sampling. The sample is used as the IR source. The radiation emitted from the surface of the sample is collected and passed through the interferometer to the detector which is now in place of the IR source. The emission spectrum is a plot of emittance versus frequency. It is similar to the transmission spectrum, but inverted. A black body is typically used as reference background. The emission method may also be applied to powdered samples or surface analysis, however, in laboratory, transmission measurement is typically preferred.

Photoacoustic

Photoacoustic is a useful technique for samples which cannot be analyzed by other method. It requires longer sampling time and demands more sample handling effort. When IR radiation strikes the sample, some of the energy is absorbed by the sample, the sample transfers some of the heat to the ambient gas which results in a pressure wave. The pressure wave is then detected by a microphone, amplified and sent to the IR detector. No sample dilution is required for photoacoustic spectroscopy. Carbon black is used as reference background.

Microsampling

When sample quantity is limited, standard sampling techniques will not be possible. In such case, micro-sampling techniques must be applied. FTIR microscopes and many micro-sampling accessories are available to accommodate a variety of sample types.

Beam Condenser: The basic function of a beam condenser is to reduce the size of the energy beam, focus it on the sample, and then return it to its normal size before entering the spectrometer. Most beam condensers offer a variety of sample holders for any sample phase.

Micro-KBr pellets: Dies are available for making micro pellets as small as 0.5mm for samples with limited quantity. Preparation must be taken carefully to prevent contamination of the sample. Micro-KBr pellets can be analyzed by direct transmission, however, they can be inserted in a beam condenser accessory to obtain higher signal throughput.

Diamond anvil cell: The cell is a high pressure device which is fitted with diamond windows ranging from 0.25 to 1.5mm^2 surface area. The sample is placed directly on one of the diamond face. The diamonds are then pressed together lightly sandwiching the sample in between. Since the diamonds transmit only 5 to 6% of total beam energy, it is highly recommended to use with a beam condenser or with a microscope. Useable infrared regions for the diamond cell are from 200-1800cm^{-1} and 2700-4000cm^{-1}. This technique is especially suitable for paints, plastics, fibers and other hard or elastic materials which would be difficult or impossible to preprare in KBr.

FTIR Microscope: Most FTIR microscopes provide precise infrared analysis of various size samples, down to the nanogram level. This technique is nondestructive and requires little sample preparation. The user directly views the sample and selects the area of interest by closing down the aperture. The area visually selected will be the same as that detected by the infrared detector. Microscopes are available in both transmission and reflection configurations for general purpose microsampling. The method is ideal for small particle contaminants and forensic analysis.