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FTIR
TALK
LETTER

vol. 1

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On the publication of the FTIR Talk Letter

Analytical Applications Department,
Analytical & Measuring Instruments Division

Senior Manager Takashi Hine

We at Shimadzu appreciate the confidence you show in using our company's products. At the present time, we have begun publication of an informational bulletin on the topic of Fourier Transform Infrared (FTIR) spectrometer, the "FTIR TALK LETTER".

The advances in FTIR during the past decade have warranted further attention from the Japanese Industrial Standards (JIS) and the Japanese Pharmacopeia organizations.

The JIS analytical general rules for an infrared spectrophotometer were established in 1966, which indicates the spectrophotometer is an old instrument that has been utilized for a long time. In addition to the prism spectrograph used up until that time, JIS K0117-1979 (1979) adopted spectrophotometers that use both diffraction gratings and the attenuated total reflection (ATR) method technique. The introduction of FTIR to the main body of JIS K0117-1990 (1990) was finally approved after hesitation in the past. Later, a draft was submitted in 1997, and is now in force in JIS K0117-2000 (2000).

The only infrared spectrophotometer specified in the Japanese Pharmacopeia through the 11th Edition was the double beam system. Starting in the first Supplement to the 12th Edition (1993), the use of the FTIR became officially recognized along with the use of total reflection, diffuse reflectance, and the KBr pellet method. These subsequently adopted by the USP, EP and BP.

When looking back on the advancements in construction and design, the hardware configuration in the original FTIR was somewhat different from that of today's instrument. For example, early FTIRs used an air bearing in the interferometer in addition to a double-beam optical configuration. Most of these instruments adopted special-purpose data processors (DSPs) to increase computational speed which ultimately improved data processing capabilities. Currently, personal computers (PCs) provide satisfactory computational speeds and are the processors of choice for almost all FTIR manufacturers. The S/N ratio, which ultimately determines sensitivity, of current instruments is vastly improved when compared with earlier systems. These advances have taken place due changes in the type of light sources and improvements in the interferometer and the detector.

The most significant development in terms of accessories is the infrared microscope. Our earliest model was a redesign of our optical microscope. We have actually developed and commercialized our newest model from scratch. As the culmination of an aggressive product development program, we are proud to announce the first automated infrared microscope, the Shimadzu AIM-8000. It provides users advanced high-end functionality and a PC-controlled aperture that regulates the measurement point.

FTIR systems are considered to be the fastest evolving instruments in the spectroscopic measurement field and that evolution is expected to continue. Manufacturers in the field are pursuing instruments which provide higher sensitivity, higher-end functionality. This will allow FTIR systems to becoming more user-friendly while offering a broader scope of applications.

It is our intent for "FTIR TALK LETTER" to serve as a useful information resource as well as a forum for exchange. Thank you again for continuing to be one of our valued customers.

How to Read Power Spectra No.1

～Measurement Region～

Spectroscopy Business Unit, Analytical & Measuring Instruments Division Hiroshi Ota

In Fourier transform infrared spectrometers, a background measurement is casually made before the sample measurement. However, if this measurement will be made carefully, you can obtain more satisfactory measurements.

First, start up the IR Solution program. Next, establish the link between the FTIR instrument and the computer. Now select the 'Measurement' tab and check the box beside 'Display Background (K)' (Fig. 1) to carry out a background measurement.

Fig. 2 shows the background measurement taken with the standard parameters. The result is referred to as a Power Spectrum because the actual signal intensity distribution is displayed for each wavelength. The final transmission spectrum of a sample is obtained by dividing power spectrum of the sample measurement by that of background measurement. The data obtained for those wavenumbers with a stronger signal intensity will have less noise.
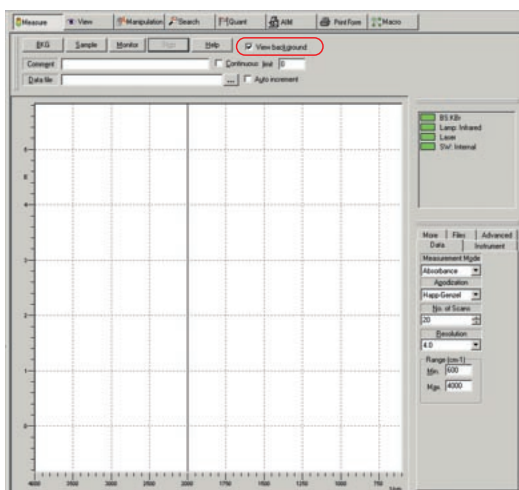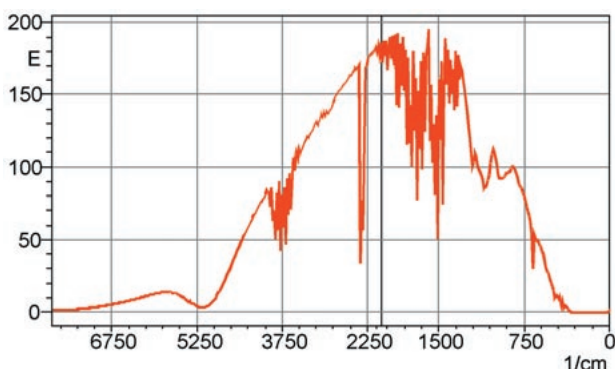

Figure 1 Measurement screen

Figure 2 Power Spectrum of Background Measurement

From the Power Spectrum, the measurement region and the level of noise in that region are identified. Looking at the spectrum in Figure 2, the signal intensity in the vicinity of 2000 cm^{-1} is strong and then becomes weaker on either side of this value. On the long wavelength side, the signal reaches almost zero at 350 cm^{-1}, which indicates that measurements cannot be made at longer wavelengths (0-350 cm^{-1}). On the short wavelength side, the intensity gradually drops off until approximately 5200 cm^{-1} and then rises again in the region around 5800 cm^{-1}. It then gradually decreases up to 7800 cm^{-1} but never completely reaching zero.

The S/N ratio will be better in the wavelength regions where the signal intensity is stronger. Therefore, the best S/N will be obtained in the vicinity of 2000 cm^{-1}. The ratio will obviously decrease in the vicinity of 400 cm^{-1} and shorter than 5000 cm^{-1}. You can confirm that a measurement can be made in the region of 350-7800 cm^{-1} under these conditions from the entire Power Spectrum.

The following factors will affect changes in the intensity at individual wavelengths in these Power Spectra.

(1) Type and luminosity of the light source
(2) Material of the beam splitter
(3) Window in the sealing case of the interferometer
(4) Type of infrared detector and window
(5) Internal amplifier filter
(6) Accessories used

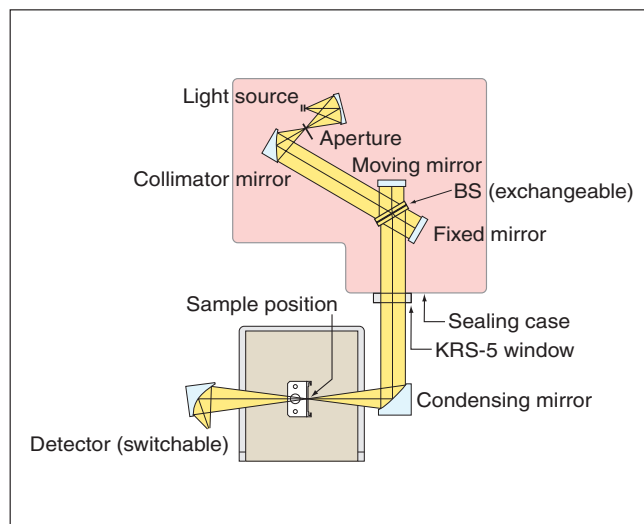We will now discuss the effects of the individual factors on the spectral intensity.

Figure 3 Schematic diagram of the IRPrestige-21 optical system

(1) Type and luminosity of the light source

A high-luminosity ceramic is used as the infrared light source in the IRPrestige-21 and the FTIR-8400S. The luminosity of approximately 1200°C is held constant over time by both an applied voltage control system in the lighting up circuit and a heater unit enclosed in the ceramic. The heater unit has a long operational life ensuring the durability of the high surface temperature.

Bodies that emit light at all wavelengths are referred to as black body radiators. The emission of the ceramic light source may be approximated as pseudo-black body radiator. The spectral distribution for the light source can be determined from the Planck's Radiation Law or the Planck Radiation Formula:

$$U(v)dv = \frac{8\pi h}{c^3} \frac{1}{\exp(hv/kT) - 1} v^3 dv \qquad (A)$$

Note) c = speed of light in a vacuum; k = Boltzmann's Constant; h = Planck's Constant

(2) Material of the beam splitter

For the middle infrared region, germanium is used for the beam splitter. The extremely thin nature of the beam splitter, with a thickness measured in microns, dictates that the germanium be deposited by vapor-deposition on IR-transparent material (e.g., potassium bromide).

IR-transparent materials are various substances that do not absorb light in the IR region of the electromagnetic spectrum.

(3) Aperture plate interferometer casing

When the humidity increases inside the interferometer deliquescence occurs which ultimately hinders the unit from being used for measurements. Deliquescence is the phenomenon by which crystals absorb moisture, swell, and undergo breakdown. In a climate with high temperatures and high humidity, it is important to take adequate steps against deliquescence within the FTIR.

KRS-5 is used as the exit aperture plate for the airtight interferometer casing in the FTIR-8400S and IRPrestige-21 because of its excellent moisture resistance. Our KRS-5 aperture plate possesses the following characteristics:

Wavelength transmission region: 16600-250 cm⁻¹
Transmittance: 70 %T

The KRS-5 plate was adopted for use in the present instrument because the increased reliability with respect to moisture out weighed the loss of throughput (30 %).

(4) Infrared detector and aperture plate

Standard infrared detectors are equipped with a DLATGS pyroelectric element. The designation comes from an abbreviation that stands for deuterated L-alanine triglycine sulfate. Since the properties of the DLATGS elements change with temperature, the temperature is controlled to maintain stable sensitivity.

Moreover, since these DLATGS elements can undergo deliquescence, a KRS-5 aperture plate is used to block out external air.

When the signal from the incoming infrared light changes rapidly, the DLATGS element has the property (frequency dependence) that allows it to decreases the output signal strength. Consequently, if the mirror speed is increases to 9.0 mm/s from the usual rate of 2.8 mm/s, the signal output will decrease and the power spectrum intensity will drop to 1/3 of the normal level.

Another option is to install the MCT quantum detector which does not display as large of a frequency dependence as the DLATGS detector. Therefore, there will be less dramatic decrease in the output signal, when the mirror speed is set to 9.0 mm/s. This is the main reason that this high sensitive detector is utilized in an infrared microscope for measurements and time-variable measurements that require high speed.

However, the MCT quantum detector requires cooling with liquid nitrogen. It also displays a drop in sensitivity in the vicinity of 700 cm⁻¹ and drops nearly to zero on the longer wavelength (lower wavenumber) side.

(5) Internal amplifier filter

Electronic amplification is important for processing the infrared interference signal input from the detector. First, the signal from the low wavenumber side (long wavelength side) is run through a high-pass filter in order to remove noise due to commercial frequencies (60 Hz and 50 Hz), and then a low-pass filter is used on the signal from the high wavenumber side (short wavelength side) in order to avoid folding (overlapping) due to the sampling theorem.

(6) Accessories used

The measurement region can also be limited by the accessories used. For example, when utilizing the ATR technique, the measurement region is intrinsically limited by the material of the prism.

In addition, for accessories that employ infrared transmission aperture plates (e.g., liquid cells, solid cells, and gas cells) each of the various materials used can have a different transmission range and transmittance. Care should be taken to ensure that the intensity distribution will be satisfactory prior to making the measurement.

Substance	Wavelength region	Transmittance (thickness)
Germanium (Ge)	5500-660 cm⁻¹	50 %T (2mm)
Zinc selenide (ZnSe)	10000-500 cm⁻¹	65 %T (1mm)
KRS-5 (note)	16600-250 cm⁻¹	70 %T (2mm)
Potassium bromide (KBr)	40000-340 cm⁻¹	90 %T (5mm)
Sodium chloride (NaCl)	50000-600 cm⁻¹	90 %T (5mm)
Diamond	40000-30 cm⁻¹	70 %T (1mm)
Potassium chloride (KCl)	40000-500 cm⁻¹	90 %T (10mm)

＊Note) KRS-5 is a mixed crystal of thallium bromide and thallium iodide.

ATR Precautions

No.1

Tokyo Customer Support Center,
Analytical Applications Department,
Analytical & Measuring Instruments Division

Tsuyoshi Tsuchibuchi

The ATR technique (attenuated total reflection and internal reflection) is attractive to a wide range of application (e.g., films, rubber, polymers and liquid samples) because sample pretreatment is unnecessary to obtain information from the surface of the sample. This advantage was further utilized through the incorporation of the ATR objective lens in a microscope and the single-reflection ATR measurement accessory in the bench-top FTIR. These advancements have made it possible to obtain measurements with minimal operator effort and with good sensitivity for minute samples in microscopic regions, those with rough surfaces where adhesion to the prism would be detrimental, curved samples, and powdery samples.

The effects, of the ATR technique, on a sample spectrum are well characterized. For example, the depth of penetration is inversely proportional to increasing wavelength. Therefore, the peak intensity generally decreases as one proceeds from the low wavelength to the high wavelength side of a spectrum. In samples that possess a high refractive index one may observe peak distortion, skewed baselines, and shifts in both the peak positions and the peak intensity in the spectrum.

1. Partial peak shifts due to types of prisms

It is well known that the ATR spectra of samples with high refractive indices show peak distortion and peak shift to lower wavenumber side compared to transmission spectra. However, the same sort of phenomenon also occurs to some extent in the ATR spectra of substances that have a refractive index of approximately 1.5 (e.g., resins).

Figures 1 & 2 show the results of measurements of PET (poly(ethylene terephthalate)) films with the MIRacle single-reflection ATR accessory. The measurements were where taken with both ZnSe (refractive index = 2.4, Fig. 1) and Ge (refractive index = 4.0, Fig. 2) prisms using a resolution of 2 cm-1 and 40 scans.

While comparing the two spectra, the relatively small peaks at 1505.51, 1340.58, and 871.86 cm-1 are consistent. However, there is clearly differences in the large peaks in the vicinity of 1712, 1244, and 1096 cm-1. This is a result of the ZnSe prism shifting the peaks toward the low wavenumber side. In addition, the positions of the peaks at 724.30 cm^{-1} overlap in wavenumber but clearly possess different widths.

The change in width is attributed to the change in refractive index as a function of wavenumbers. The changes are more prominent in the case of strong absorption. So the opposite is also true. In cases where the prisms used have a relatively small refractive index (e.g., ZnSe and diamond (refrective index) = 2.4) this effect is less evident. As an example, we compare results obtained with a ZnSe prism to that obtained with a Ge prism (refractive index = 4.0).
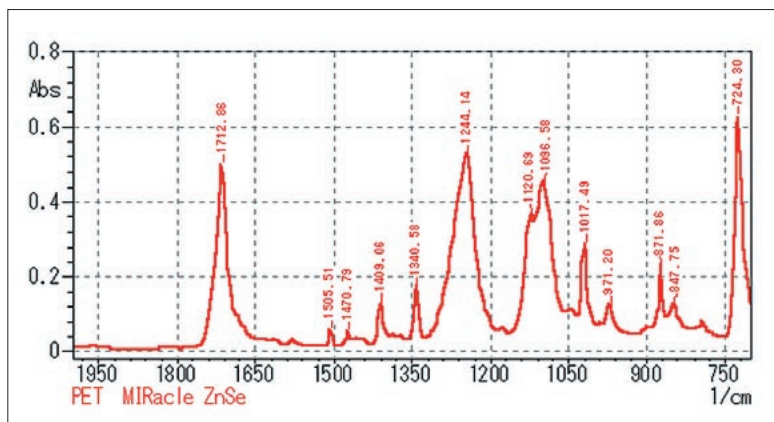

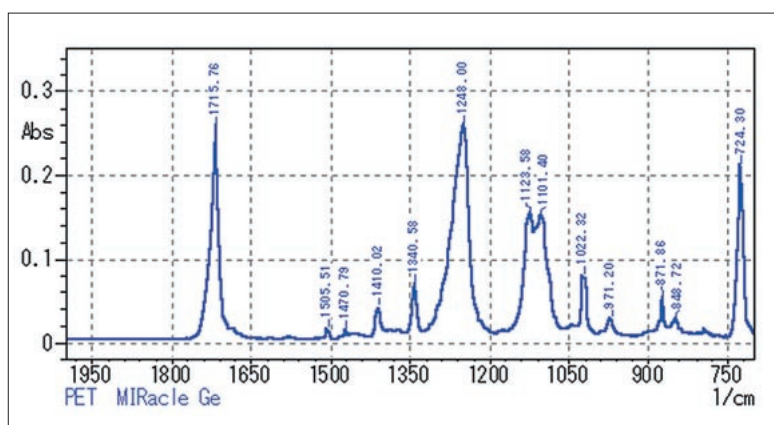Figure 1 ATR Spectrum of PET (prism: ZnSe)

Figure 2 ATR Spectrum of PET (prism: Ge)

2. Effect of physical changes in the sample as a result of pressure

When using the ATR technique to measure solid samples, it is necessary to press the sample against the prism. If there is any change in the physical state of the sample due to pressure, these changes will be manifested in spectrum obtained. Fig. 3 presents the spectra of low density polyethylene collected on a DuraSampl-IR single-reflection ATR, at three different pressures.

It is clear from Fig. 3 that the peak in the vicinity of 1472 cm^{-1} increases as pressure is increased. In contrast, the peak in the vicinity of 1462 cm^{-1} decreases as the pressure is increased. Despite these subtle differences, we can conclude that there is no substantial difference occurring in the area between the prism and the sample as a function of pressure.

Both peaks are assigned to CH_2 scissor vibrations, but the peak in the vicinity of 1472 cm^{-1} is attributed to crystalline regions in the sample. Pressing the sample against the prism with strong pressure has been shown to cause changes in the sample's properties such as its crystallinity.

During ATR measurements, tight adhesion is necessary between the sample and the prism in the ATR. But one most always keep in mind that the sample measurement is affected by this act of "pressing" and realize that this effect can result in minute differences and changes between samples.
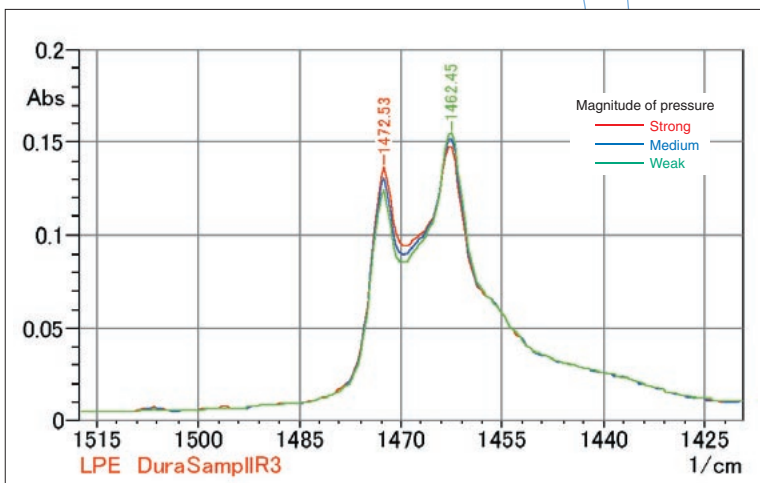

Figure 3 ATR Spectra of low density polyethylene vs. pressure.

3. Conclusion

The previous discussion serves as an introduction to the effects of refractive index, wavenumber, and differences in pressure on a spectrum. The next installment, "ATR Precautions - No. 2", will serve as an introduction to the effect of sample adhesion between the sample and the prism on a spectrum.
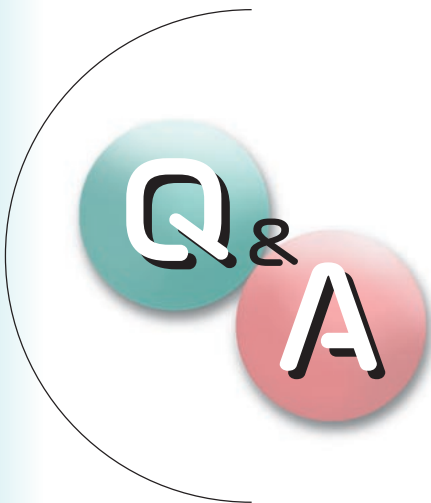
When making a measurement using the ATR technique, how deeply does the infrared light penetrate in the region of sample and prism contact?

Answer

When using the ATR technique, the factors affecting how deeply the light penetrates are: (1) Wavenumber, (2) Incident angle, and (3) Refractive index. The following equation takes into account all three factors for determining the depth of penetration in the region of sample adhesion:

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

where θ is the incident angle of the infrared light, n_1 and n_2 are the refractive indices of the sample and the prism, respectively.

(1) Wavenumber
From the above equation, the penetration will be deeper at lower wavenumbers when compared to the spectra obtained with the transmission technique as shown in Fig 1. Therefore, the peak intensities in the spectrum obtained will become unusually strong on the low wavenumber side.

(2) Incident angle
The larger the incident angle, the more shallow the penetration.

(3) Refractive index
When measurements are taken of a sample using prisms of different refractive index, the penetration will be shallower when the measurement is taken with a prism having a higher refractive index. Moreover, it is possible to use the above equation to make a theoretical calculation of the penetration depth of the light.

In the theoretical calculation, an incidence angle of 45° and the refractive index of common organic compounds, (n_1 = 1.50), are used. Taking the case of multiple layer film containing layers of different materials, the peak obtained may vary according to the selection of prism.

Results of the theoretical calculation for the depth of penetration

Wavenumber/cm^{-1}	Prism (refractive index)	
	ZnSe or KRS-5 (2.4)	Ge (4.0)
4000	0.50 μm	0.17 μm
3000	0.66 μm	0.22 μm
2000	1.01 μm	0.33 μm
1500	1.35 μm	0.44 μm
1000	2.01 μm	0.66 μm
400	5.03 μm	1.66 μm

Saccharose KBr pellet method

Saccharose Single-reflection ATR technique
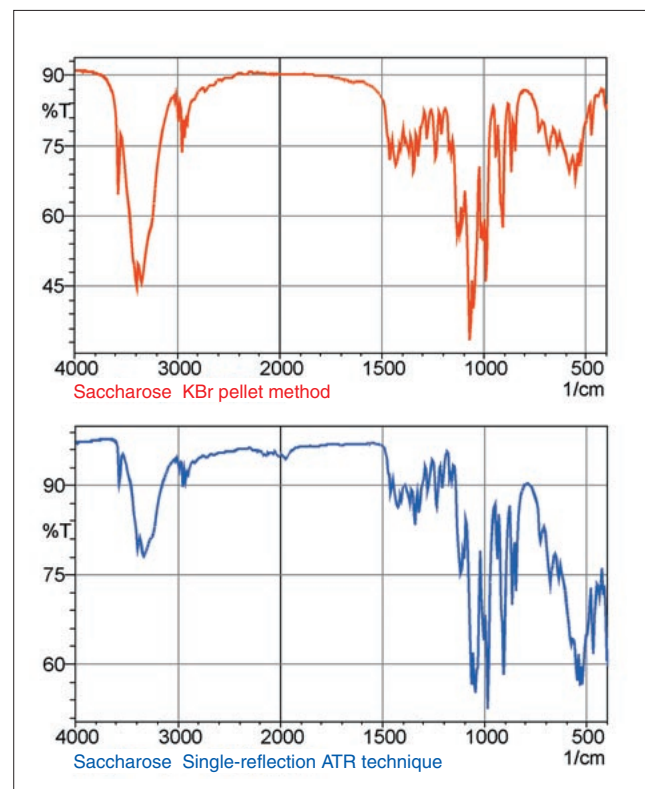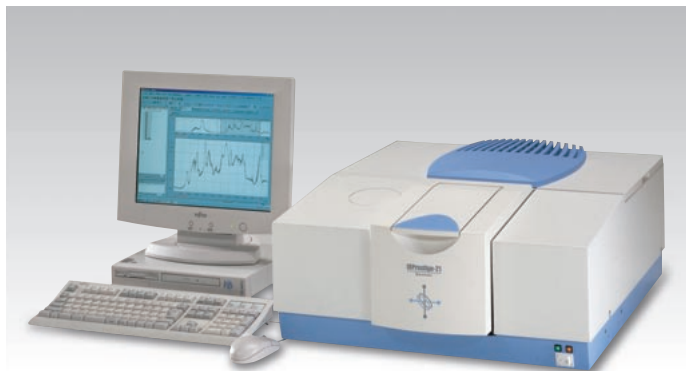
Figure 1 Comparison of transmission vs. ATR techniques (Top: transmission; Below: ATR)

Shimadzu FTIR Family

IRPrestige-21

'Next-generation' FTIR can be retro-fit with kits which cover the near to far infrared, while still maintaining top-class sensitivity and providing FDA 21 CFR support.

- **Signal to Noise Ratio: 40,000:1**
- **Interferometer:**
  Michelson interferometer, incorporating dynamic alignment
- **Detector: DLATGS detector with temperature control**
- **Resolution: 0.5, 1, 2, 4, 8, 16 cm^{-1}**

Fourier Transform Infrared Spectrophotometer

FTIR-8400S

Highly sensitive and easy to operate. Incorporates dynamic alignment to maintain optimal interference. Validation programs and data processing functions for searching and quantitation are standard with each instrument.

- **Signal to Noise Ratio: 20,000:1**
- **Interferometer:**
  Michelson interferometer, incorporating dynamic alignment
- **Detector: DLATGS detector with temperature control**
- **Resolution: 0.85, 1, 2, 4, 8, 16 cm^{-1}**
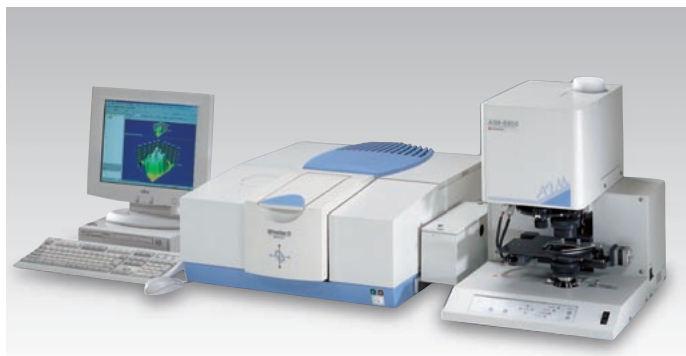
Fourier Transform Infrared Spectrophotometer

FTIR Microscope

Excellent sensitivity is achieved by adopting a high-efficiency reflecting objective mirror and aspheric mirrors for an optimized optical configuration. Ease of operation is aided by the ability to control of stage movements, aperture settings, and focusing from the PC screen.

- **Fourier Transform Infrared Spectrophotometer**
  (FTIR-8000 Series (except 8100), IRPrestige-21)
- **IR Microscope AIM-8800**

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