Optical spectroscopy is one of the most powerful and widely used methods for material identification and analysis. There are six basic spectroscopic techniques: transmission, internal reflection or ATR, external reflection, diffuse reflection, emission, and photoacoustic. These techniques are employed over a broad spectral range from the ultraviolet to the far infrared.
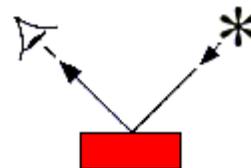
Transmission Spectroscopy
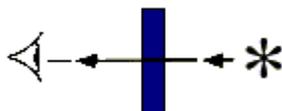
This technique can be used for solid, liquid, and gas sampling. Here, light is passed through the sample and compared to light that has not. The resulting spectrum depends on the pathlength or sample thickness, the absorption coefficient of the sample, the reflectivity of the sample, the angle of incidence, the polarization of the incident radiation, and, for particulate matter, on particle size and orientation.

Transmission spectroscopy was the only method in general use until the early 1960s. Thus large libraries of transmission spectra are readily available. These are frequently used for comparision of spectra obtained by other techniques, even though the frequency response differs between techniques.

External Reflection Spectroscopy

In this technique, also known as specular reflectance, light is reflected from a smooth (mirror-like) sample to record its spectrum. External reflectance was analyzed theoretically as a spectroscopic technique for films on mirror surfaces by Francis and Elison in 1959. Some applications followed in the mid-sixties and the technique found much wider use in the 1970s when accessories became more readily available. External reflectance is a non-destructive, non-contact technique. It is particularly useful for film thickness and refractive index measurements, as well as recording spectra of thin films on metal substrates.

External reflection spectra may look different from transmission spectra in many ways, e.g. bands may be shifted to higher wavenumbers, spectra may follow the dispersion in the refractive index, and spectral contrast may not depend linearly on sample thickness.

Internal Reflection Spectroscopy (ATR)
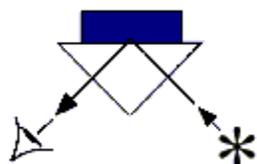
For ATR, light is introduced into a suitable prism at an angle exceeding the critical angle for internal reflection. This produces an evanescent wave at the reflecting surface. A sample is brought in contact with or in close proximity to the reflecting surface. From the interaction of the evanescent wave with the sample, a spectrum can be recorded with little or no sample preparation. The ATR technique is non-destructive and can be used for solids, liquids, and powders. This technique was introduced in the 1960s and is now widely used.

For thin films, the ATR spectra are the same as transmission spectra. For thick films, the absorption bands are more intense at longer wavelengths. As the angle of incidence approaches the critical angle, the bands tend to broaden on the long wavelength side and the minima are displaced to longer wavelengths (lower wavenumbers). Dispersion type spectra are observed very close to and below critical angle.

Diffuse Reflection Spectroscopy

Spectra of powders and rough surfaces can be recorded by illuminating these surfaces and, with the aid of the appropriate optics, collecting sufficient scattered light for spectral analysis. This has been done routinely in the UV-VIS with integrating spheres and in the infrared with
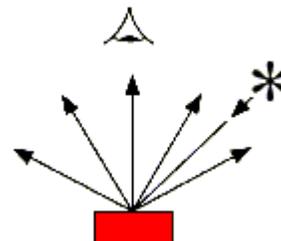
ellipsoids and paraboloids to collect the scattered radiation. Reaction chambers for diffuse reflectance allow the study of catalysis and oxidation reactions in situ.

Since diffuse reflection spectra are the result of the interaction of light with the sample in every conceivable way, the spectra may exhibit features of transmission, external reflection, and/or internal reflection. One bothersome feature is the presence of reststrahlen bands whose contrast can be reduced by sample dilution. In addition, sample particle size and angle of illumination and/or observation can affect the observed spectra.

Emission Spectroscopy
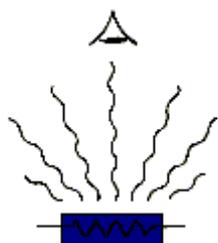
In emission spectroscopy, the radiation emitted by the sample is measured. If room temperature detectors are used, the sample must be heated or cooled; with low temperature detectors, the sample may remain at room temperature. Emission is a non-destructive sampling technique and is particularly useful for films on rough metal surfaces and catalysis studies. Emission can be used in some areas where all other techniques fail, e.g. recording spectra of impurities in microscopic craters and crevices.

Emission spectra are also affected by the nature of the sample, e.g. particle size which controls the surface to volume ratio and concentration which controls reabsorption of emitted radiation and tends to invert emission peaks. Adsorption bands tend to be narrower in emission than in transmission or diffuse reflection. In a few cases, selective reflection is responsible for inversion of peaks. This arises from the situation where in the expression for emissivity, $E=1-T-R$, the reflectivity at certain frequencies is not low enough to be neglected.

Photoacoustic Spectroscopy

In this technique, the sample literally 'talks' to the observer. Light entering the photoacoustic cell passes through undetected if the sample is non-absorbing, but heats and expands the gas in the cell if the light is absorbed. This expansion (and subsequent contraction) of the gas makes an audible sound whenever absorption occurs. This sound is detected by a microphone. Photoacoustic is a non-destruction sampling technique. Its spectra are not dependent on sample size or shape, and band shifts and artifacts like reststrahlen bands are absent. The signal to noise ratio may increase with sample surface area. Sample loading and unloading can be tedious. Photoacoustic spectroscopy is particularly sensitive to interfering spectra from evolved gases. Extreme caution must be exercised to minimize vibration of the apparatus.
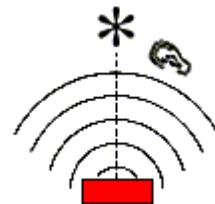
Since the spectrum obtained by the photoacoustic technique is a direct measure of the absorption of radiation by the sample, some of the optical problems such as interference fringes and reststrahlen bands are absent. On the other hand, the detection of pressure waves is related to properties such as thermal diffusivity which can vary between samples. Therefore, comparison of spectra between different types of samples is not as straightforward as with other techniques. Furthermore, techniques such as depth profiling by changing scanning speeds is very difficult. This is because the thermal diffusivity is not necessarily constant with sample depth.