

UV-Visible and IR Spectroscopy

To study Catalyst surfaces

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UV-Visible Diffuse Reflectance spectroscopy

The governing principle of DR UV-Vis spectroscopy is the same as that of UV-Vis absorption. When a beam of monochromatic light impinges on the surface of powder, a part of the beam is absorbed, some undergoes specular reflection (mirror reflection) and a part of the beam is scattered.

Mirror or specular reflectance is observed when the angle of incident radiation and the angle of reflected radiation are equal.

Diffuse reflectance is the reflected radiant energy that has been partially absorbed, transmitted and partially scattered by a surface. For solid surfaces we need to measure the intensity of the scattered radiation, since the absorbance cannot be measured in case of solids.

The basic components of a DR UV-Vis spectrophotometer are as follows:

- A Light source (deuterium, halogen, xenon, or LED lamps)
- Monochromator
- Lens
- Integrating sphere
- Sample holders
- Detector

1. Light Source:

There are various light sources for UV-Vis spectrophotometer:

Deuterium lamps have wavelengths of the range 190nm-370nm. To cover the visible spectrum, halogen lamps are also used with it. Because of its high temperature behavior, normal glass housing cannot be used but requires quartz or MgF₂ casing.

Halogen lamps cover the entire visible spectrum (320-1100nm). They cover only the visible region.

Xenon lamps reach steady state in shorter time. It covers the entire UV-visible spectrum 190-1100 nm.

LED light source produces a single wavelength of light so no monochromator is needed.

2. Monochromator

The monochromator comprises a dispersive element, an entrance slit and mirrors to create a parallel beam similar to sunlight, and an exit slit and mirrors to extract the monochromatic light.

Prism and diffraction gratings are the typical dispersive elements. Diffraction gratings are used due to their superior dispersion. The prism achieves dispersion due to the difference in the material refractive index according to the wavelength. However, the diffraction grating uses the difference in diffraction direction for each wavelength due to interference.

3. Integrating Sphere

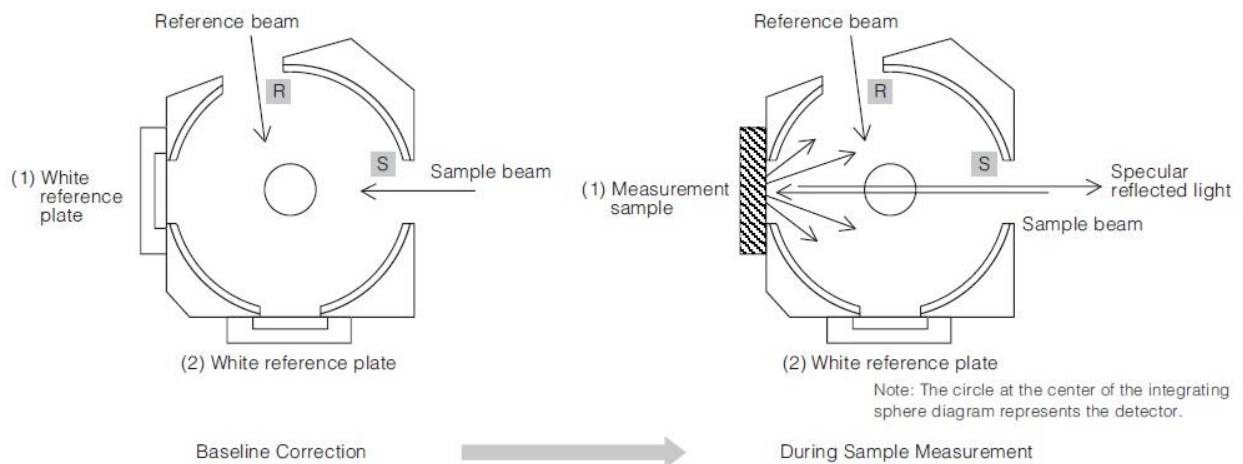
Integrating spheres have spherical inner surface which is coated with highly reflective material is Barium Sulfate or Magnesium oxide. Integrating spheres are effective in scattering entering light uniformly. Regular detectors detect the measurement light that hits the light-sensitive surface of the detector. However, light that is scattered after the sample is irradiated protrudes from the light-sensitive surface of the detector, thus preventing correct measurement. When an integrating sphere is used to measure a sample, correct measurement can be performed since all measurement lights are irradiated on the light-sensitive surface of the detector after being diffused inside the integrating sphere at both baseline correction and sample measurement.

A monochromatic light may cover a certain range of wavelengths. For ex. A 540 nm light may extend from 539.5 nm to 540 nm. Then this monochromator is said to have 1nm resolution. The smaller the bandwidth, the better is the resolution. The resolution is measured by **Peak Width at Half Maximum (PWHM)**. The resolution is determined by the slit width. A wider slit produces a larger image at the exit. Diffraction gratings have an inherent resolution which is the number of gratings.

4. Baseline measurement

The baseline measurement is performed with standard sample like white board filled with Barium sulfate and it is irradiated with the light passing through the aperture. After the baseline is measured, the standard sample is replaced with the sample whose diffuse reflectance is to be measured. This type of reflectance using an integrating sphere is called as **Relative Reflectance** since reflectance is measured with respect to standard sample. This means that the reflectance changes when the sample is changed.

$$\text{Relative Reflectance} = \frac{\text{Amount of light reflected from the sample}}{\text{Amount of light reflected from reference plate}} \times 100$$



5. Measuring Diffuse and Total Reflectance

For diffuse reflectance, a normal measurement light (0° angle) is irradiated on the sample. The diffused reflectance component is diffused inside the integrating sphere and the specular reflectance component exists outside the integrating sphere. So, only the diffuse reflectance is measured in this case (*fig 1*).

For total reflectance measurement, the measurement light is irradiated at an angle approximately 8° tilted with respect to the sample. In this measurement, the diffuse reflectance component is diffused in the integrating sphere along with the specular component as it strikes the integrating sphere's wall. So, in this case both diffuse and specular reflectance is measured (*fig2*).

Since the intensity of the diffuse reflectance component is in the order of $1/1000^{\text{th}}$ of the measurement light with the measurement light being directly received by the detector, the noise increases. To reduce noise, the intensity must

be reduced. This is achieved by widening the slit of spectrophotometer. Usually the integrating spheres have 60mm inner dia. Some have 150mm inner dia but have smaller aperture ratio. But due to greater space inside the integrating sphere, the intensity of the light at the detector decreases due to increased noise.

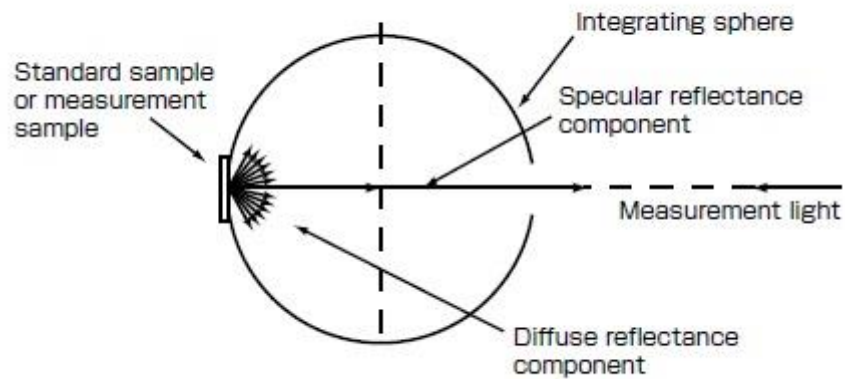


Fig. 1 Diffuse Reflectance Measurement

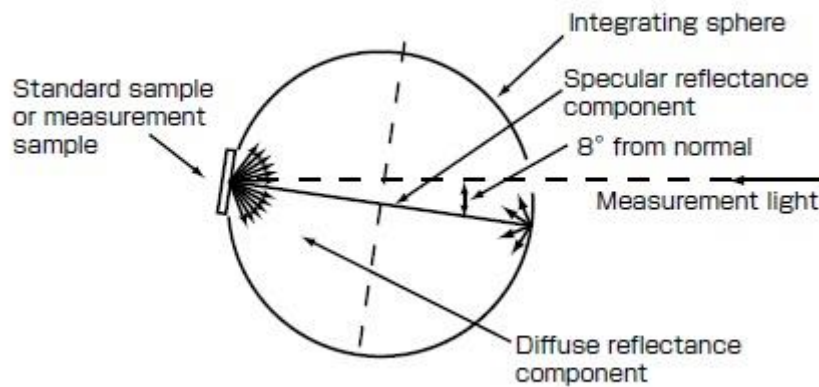


Fig. 2 Total Reflectance Measurement

$$\text{Aperture Ratio} = \frac{\text{Area of the hole}}{\text{Total area of the integrating sphere}}$$

6. Sample Holders

Basically, two types of sample holders are used:

1. Center-mount cuvette style sample holder.
2. Clip and jaw style sample holder.

Center-mount type is used for turbid samples. Only transmittance can be measured.

Clip type uses a spring-loaded clip to hold the sample. Jaw type holder is suitable for holding bulky samples. This type of holder is designed for samples that reflect light (opaque).

7. Detector

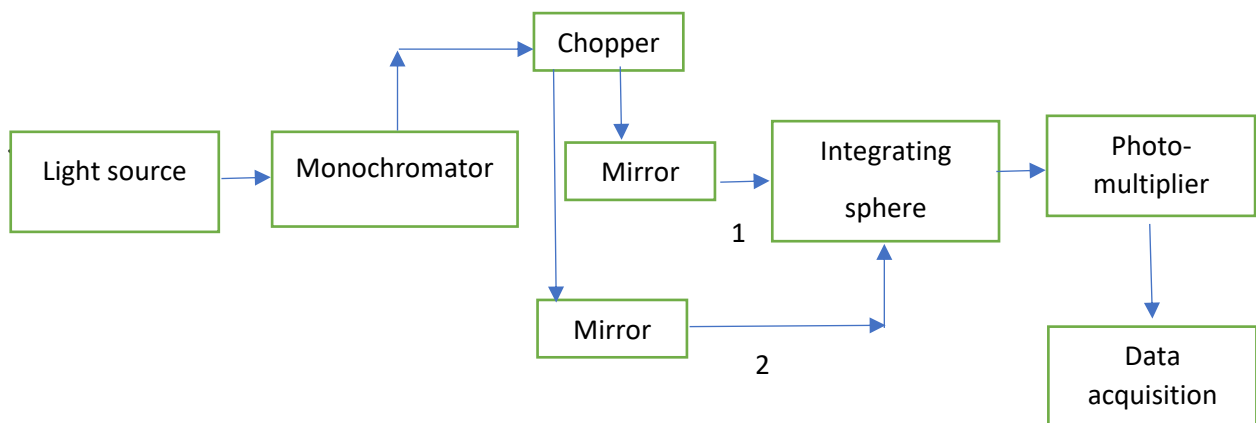
7.1 Photo-Multiplier Tube

A photomultiplier is a detector that uses the fact that photoelectrons are discharged from a photoelectric surface when it is subjected to light (i.e., the external photoelectric effect). The photoelectrons emitted from the photoelectric surface repeatedly cause secondary electron emission in sequentially arranged dynodes, ultimately producing a large output for a relatively small light intensity. The most important feature of a photomultiplier is that it achieves a significantly high level of sensitivity that cannot be obtained with other optical sensors. If there is sufficient light intensity, this feature is not particularly relevant, but as the light intensity decreases, this feature becomes increasingly useful. For this reason, photomultipliers are used in high-grade instruments.

7.2 Silicon Photo Diode

A silicon photodiode is a detector that uses the fact that the electrical properties of a detector change when it is exposed to light (i.e., the internal photoelectric effect).

In comparison with photomultipliers, silicon photodiodes offer advantages such as low cost, little locality of sensitivity in the light-receiving surface, and the fact that a special power supply is not required. Even regarding sensitivity, if the light intensity is relatively large, they can obtain photometric data that is no inferior to that obtained with photomultipliers.



Basic components of UV-Vis DR spectrophotometer

Beam 1-sample beam

Beam 2-Reference beam

Infra-Red spectroscopy for characterizing solids

Light sources for IR:

Instruments for measuring infrared absorption all require a source of continuous infrared radiation and a sensitive infrared transducer, or detector. Infrared sources consist of an inert solid that is electrically heated to a temperature between 1,500 and 2,200 K. The heated material will then emit infra-red radiation.

The Nernst glower

The Nernst glower is constructed of rare earth oxides in the form of a hollow cylinder. Platinum leads at the ends of the cylinder permit the passage of electricity. Nernst glowers are fragile. They have a large negative temperature coefficient of electrical resistance and must be preheated to be conductive.

The global source

A global is a rod of silicon carbide (5 mm diameter, 50 mm long) which is electrically heated to about 1,500 K. Water cooling of the electrical contacts is needed to prevent arcing. The spectral output is comparable with the Nernst glower, except at short wavelengths (less than 5 mm) where its output becomes larger.

The carbon dioxide laser

A tuneable carbon dioxide laser is used as an infrared source for monitoring certain atmospheric pollutants and for determining absorbing species in aqueous solutions.

There are many ways to study the IR spectra of solids:

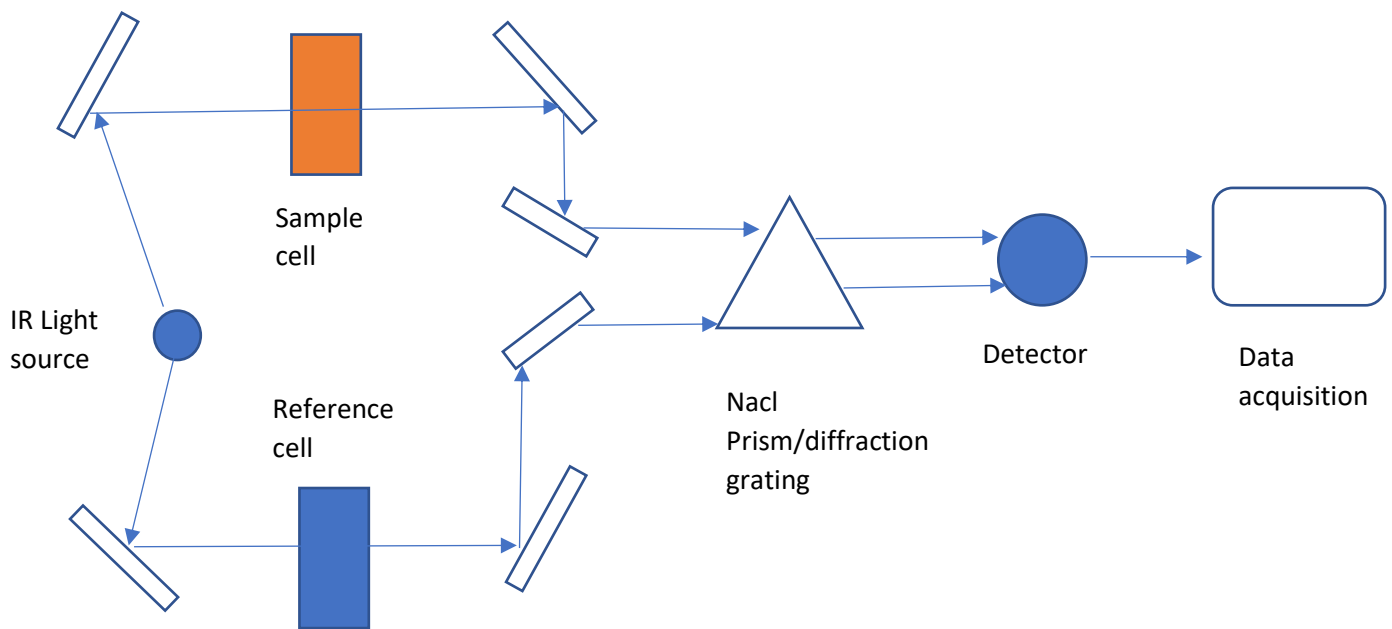
1. Solid run in solutions
2. Solid films
3. Mull technique
4. Pressed pellet technique

The above techniques involve treating the solid samples before studying them. On the other hand, *Diffuse Reflectance Infra Red Fourier Transform* spectroscopy requires little or no sample treatment.

1. Solid run in solutions: Solids are dissolved in non-aqueous solvent and a drop of this solution is placed on an alkali metal disk like and the solvent is allowed to evaporate, leaving a thin film of solid which is then mounted in spectrometer.
2. Solid films: If the solid is polymer resins or amorphous solids, the sample can be dissolved in a volatile solvent and it is poured on NaCl or KBr plate and the solvent is evaporated by heating gently.
3. Mull technique: A small quantity of the powder is finely ground in a clean mortar until the powder is very fine. Then a mulling agent like mineral oil or nujol is added in small quantity. The mixture is then transferred to mull plates and the plates are squeezed together to adjust the thickness of the sample between IR transmitting windows.
4. Pressed pellet technique: The sample is intimately mixed with about 100 times its weight with KBr in a vibrating ball mill. The mixture is then pressed under very high pressure (2500 psig) in a die 1 or 2mm thick and 1cm in diameter.

Diffuse reflectance technique is used for powders and solid samples having rough surface such as paper, cloth. In diffuse reflectance technique, particles size, homogeneity, and packing density of powdered samples play important role on the quality of spectrum. A sample with smaller particle size having narrow size distribution is preferred. Thus, in order to obtain a qualified spectrum, the sample should be ground into smaller size. In this method, the sample can be analyzed

either directly in bulk form or as dispersions in IR transparent matrices such as KBr and KCl. Sometimes, a thin film of KBr powder placed on the sample surface to improve the quality of the spectrum. Dilution of analyte in a non-absorbing matrix increases the proportion of diffuse reflectance in the reflected light. Typically, the solid sample is diluted homogeneously to 5 to 10% by weight in KBr. Diffuse reflectance measurement in near-IR is more common than in mid-IR. Because non-absorbing scattering substrates are rare in mid-IR, and also more efficient scattering occurs at shorter wavelengths (near-IR). Additionally, due to lower efficiency of the scattering in mid-IR, diffuse reflectance is very weak in this region, as a consequent, in mid-IR, diffuse reflectance could only be measured by FT-IR spectrometer (DRIFTS). In diffuse reflectance spectroscopy, diffusely scattered light can be directly, collected from material in a sampling cup or, alternatively, collected by using an abrasive sampling pad. In mid-IR, the diffusely reflected light from sample is generally collected by large ellipsoidal mirrors, which cover as much area above the sample as possible. In near-IR, diffuse reflectance spectra are usually measured by an integrating sphere, described by Ulbrich. The inner surface of "Ulbrich sphere" is coated by strongly scattering, nonabsorbing powder. After repeated reflection, all radiations reach the detector. Thus, with Ulbrich sphere the entire radiation reflected by the sample is integrated. The working principle is same as that of the UV-Vis Diffuse Reflectance spectroscopy.



IR Spectrophotometer

Detectors

Thermal detectors

Thermal detectors can be used over a wide range of wavelengths and they operate at room temperature. Their main disadvantages are slow response time and lower sensitivity relative to other types of detectors.

Thermocouple

A thermocouple consists of a pair of junctions of different metals. The potential difference (voltage) between the junctions changes according to the difference in temperature between the junctions. Several thermocouples connected in series are called a thermopile.

Bolometer

A bolometer functions by changing resistance when heated. It is constructed of strips of metals such as platinum or nickel or from a semiconductor.

Pyroelectric detectors

Pyroelectric detectors consist of a pyroelectric material which is an insulator with special thermal and electric properties. Triglycine sulphate is the most common material for pyroelectric infrared detectors. Unlike other thermal detectors the pyroelectric effect depends on the rate of change of the detector temperature rather than on the temperature itself. This allows the pyroelectric detector to operate with a much faster response time and makes these detectors the choice for Fourier transform spectrometers where rapid response is essential.

Photoconducting detectors

Photoconducting detectors are the most sensitive detectors. They rely on interactions between photons and a semiconductor. The detector consists of a thin film of a semiconductor material such as lead sulphide, mercury cadmium telluride or indium antimonide deposited on a nonconducting glass surface and sealed into an evacuated envelope to protect the semiconductor from the atmosphere. The lead sulphide detector is used for the near-infrared region of the spectrum. For mid- and far-infrared radiation the mercury cadmium telluride detector is used. It must be cooled with liquid nitrogen to minimize disturbances.