

Methods in optical spectroscopy

UV-VIS Spectroscopy

For UV-VIS spectroscopy, a wide range of possible combinations of excitation source, optics, measuring geometry and sample chamber as well as detectors are available, which can be specifically selected depending on requirements. If, for example, color values are to be determined in a defined manner, a calibrated excitation source is required. If the aim is to observe the coating thickness using interference evaluation, a goniometer may be required to set the angle of incidence and reflection of the radiation.

A special case is the mobile use of (hyperspectral) UV-VIS spectrometers, where no additional excitation is required and daylight or sunlight is used for excitation instead. In order to obtain comparable spectra, defined referencing, adjustment of the exposure times (especially in changing light conditions) and standardization of the spectra are necessary.

Optical fluorescence spectroscopy

When investigating optical fluorescence, the excitation radiation must be suppressed. In practice, this is achieved by a (detector) observation angle of 0° to the direction of the excitation radiation. Excitation takes place in the UV, blue or green spectral range with intense excitation sources - in addition to discharge lamps (e.g. xenon), lasers are also suitable for excitation. The advantages of discharge lamps are continuous emission, making it easier to change the excitation wavelength. In fluorescence spectrometers, a monochromator is usually used, which is placed in front of the sample.

Infrared (IR) spectroscopy

The instrumentation for IR spectroscopy differs significantly between the near, mid and far infrared. While lenses, optics and detectors from UV-VIS spectroscopy can still be used up to a wavelength of approx. 1000 nm, observation in the near, mid and far infrared requires the aforementioned special detectors based on InGaAs or MCT. Some of the latter also have to be cooled with liquid nitrogen. From the mid-infrared from 2500 nm, the use of special optical materials such as potassium bromide (KBr), zinc selenide (ZnSe), germanium (Ge) or silicon (Si) is mandatory, as only selected materials are permeable in this spectral range. Halogen lamps can be used for excitation up to 2500 nm, as they emit a significant proportion of the emission in the near infrared as thermal radiation. From the mid-infrared, red-hot SiC ceramics ('Globar'), for example, are used as an emission source. In general, the heat input of the IR sources must also be taken into account for sensitive samples.

Hyperspectral spectrometers are generally equipped with transmission or reflection gratings as dispersive elements; single-channel spectrometers are often designed as FT devices with interferometers.

RAMAN spectroscopy

The advantage of many RAMAN spectroscopy configurations is that information about molecular vibrations can be obtained using the simpler and cheaper technique of the visible spectral range (however, if the excitation takes place in the near infrared, corresponding detectors must also be used in RAMAN spectroscopy). In addition, RAMAN spectroscopy is insensitive to water or aqueous media compared to IR spectroscopy. However, the observed spectrum depends very much on the wavelength and intensity of the excitation radiation.

$$I \sim \nu^4 I_0 N (\partial\alpha/\partial q)^2$$

(ν frequency of the excitation radiation, I_0 intensity of the excitation radiation, N number of scattering molecules, $\partial\alpha/\partial q$ polarizability change)

For this reason, only lasers are used for excitation; common laser wavelengths are 514.5 nm (argon ions or diode) and 785 nm (NIR diode), but practically all available laser wavelengths are possible. The excitation radiation must be masked for the detector, as it is orders of magnitude more intense than RAMAN scattering. So-called notch filters or Bragg gratings are used for this, but hard-coated long-pass filters are more robust and durable. However, the latter do not allow the observation of anti-Stokes bands¹⁰, although their observation can often be dispensed with. When using the filters, a high quality (OD value) must be ensured. With inexpensive long-pass color filters, it may also be necessary to use several filters.

A competing process to RAMAN scattering is fluorescence. Due to the intense excitation of the laser, it often occurs in RAMAN spectra and prevents the observation of the RAMAN bands by superposition. The simultaneous fluorescence excitation can be avoided by changing the excitation wavelength (excitation at longer wavelengths, but the RAMAN bands can then also be significantly lower, see equation above) or by observing the anti-Stokes bands in the RAMAN spectrum.

References

¹⁰ Anti-Stokes scattering occurs when molecules are already in an excited state and this energy is added to the excitation radiation during re-emission - i.e. re-emission occurs at a higher energy/higher frequency. However, the intensity of the scattering is again 90 % lower than that of Stokes scattering.