10.3.5 Molecular absorption spectroscopy (UV/VIS)

10.3.5.1 Instrumental factors

10.3.5.1.1 Radiation sources

Pertinent factors relating to the properties of continuum radiation sources are

the *spectral distribution* defined as the variation of the *spectral radiance*, L_λ, with wavelength,

the *maximum spectral radiance*, L_λ(max), within the usable wavelength range, the wavelength at this maximum, λ_{max},

the *usable wavelength range*, defined by the lower limit λ_l and the upper limit λ_u at which the spectral radiance is a specified fraction of L_λ (max).

Continuum sources are normally used for molecular absorption measurements, whereas *spectral-line sources* are employed for wavelength calibration of a spectrometer. Examples of continuum sources commonly used are

tungsten-halogen lamps, which have a radiance temperature, T_r, of ≈ 3000 K and therefore have maximum spectral radiance at a wavelength of about 1.2 μm; they are widely used in the visible and near ultraviolet spectral region (above 330 nm),

deuterium lamps (gas-discharge lamps) which emit strongly in the UV region below 330nm; the continuous spectrum has deuterium atomic emission lines superimposed on it,

xenon arc lamps which give a continuum from below 190 nm to above 1000 nm.

Examples of spectral-line sources are

low-pressure mercury-discharge lamps, which are sometimes used for measuring absorbances at fixed wavelengths. Such lamps are also useful for wavelength calibration,

Tunable lasers with and without frequency doubling and/or Raman shifting are high intensity sources with narrow spectral bandwidths. Their use may enable the spectral apparatus to be omitted. They may be either continuous (cw) or pulsed in nature.

10.3.5.1.2 Sample compartment

Liquid samples are usually contained in *sample cells* which are placed in *sample cell holders*. Cell holders may be heated or cooled in order to control the temperature of the liquid in the sample cell.

The important characteristics of simple cells are:

cell shape, volume and cross section,

absorption path length, *b*, defined as the length of the radiation path through the absorbing medium; it is equal to the *cell path length*, *l*, in the case of single-pass cells at normal incidence of radiation,

window material (window thickness and degree of deviation from parallelism of the windows are also important).

A pair of cells with closely similar optical properties are called *matched cells*. One cell is the sample cell while the other, the *reference cell*, contains the solvent or a reference solution. In double-beam spectrometers, radiation is passed either simultaneously or alternately through the cells. In single-beam instruments the cells are moved sequentially into the radiation beam.

Gases and vapours are measured in gas cells similar to those used for liquids. Generally the cell path length is much greater. Gases at any pressure are contained in *closed cells* for measurement.

Solid samples are held in *solid-sample holders*. When solid samples are measured, difficulties may be experienced e.g. in matching the sample and reference path lengths.

Low temperature cells are required for certain applications. These may include *cooled cells*, *thermally insulated cells*, and *cold-finger cells*.

A *stopped-flow cell* comprises a small-volume absorption cell connected to a rapid mixing chamber. By the use of mirrors a *multiple-pass cell* permits multiple passage of radiation to increase the absorption path length.

A *continuous-flow cell* allow the liquid (or gaseous) sample to pass through the cell continuously while absorption measurements are made.

A *variable path length cell* is a cell whose path length can be varied either continuously or in steps by means of spacers.

10.3.5.1.3 Data acquisition and data processing

The equipment used for *data acquisition* and *data processing* can be classified according to the form of the information required. In the simplest case the output may present the

transmittance or *absorptance* in an analogue or digital form. Further processing of the output signal enables various functions of the original signal to be obtained. These include

absorbance
log absorbance
averaged spectra (with enhanced signal-to-noise ratio)
derivative spectra
with additional processing, background correction

For the fast acquisition of material, a *polychromator* utilizing a *spatially resolved detector* eg a *vidicon*, *photodiode array* or *charge transfer device* may be used. The whole detection system, including readout electronics, is called an *optical multi-channel analyser* (See also Section 10.3.2.6).