

THERMINOLOGY

It's still a widely accepted practice to call *spectropolarimeter* a modern CD spectrometer, even if it'll record only CD spectra for its lifetime. But, when equipped with the pertinent accessories, many forms of optical activity can be measured by a conventional CD spectrometer. We arranged here a list for your convenience and for better understanding of literature data:

Circular Birefringence (CB) = Optical Rotation (OR) = Optical Rotary Dispersion (ORD)

CB is the difference in *refraction* of left and right circularly polarized light.

The polarization plane of linearly polarized light (which can be decomposed into two circularly polarized components) passing through a *chiral* sample is rotated.

$$\alpha = 2\pi l (n_L - n_R) / \lambda$$

where l is pathlength and n_L and n_R are refractive indexes for left and right circularly polarized light.

Instruments measure α usually in millidegree scale.

The CD spectrometer must be equipped with an ORD accessory (various types available)

Circular Dichroism (CD)

CD is the difference in *absorption* (or *emission*, such as in CPL case, see below) of left and right circularly polarized light. Sample must be chiral.

$$\Delta A = A_L - A_R$$

where A_L and A_R are absorbance for left and right circularly polarized light.

$g = \Delta A / A$ is called anisotropy factor

where A is the regular absorbance of the sample

More frequently instruments measure CD in millidegree of ellipticity Θ , where $\Theta = 32980 \Delta A$

Circular Polarization of Luminescence (CPL)

CPL is the difference in left and right circularly polarized emission of a *chiral* luminescent molecule

$$\Delta I = I_L - I_R$$

$g_{em} = \Delta I / \frac{1}{2} (I_L + I_R)$ is called emission dissymmetry factor

In normal cases excitation beam is not polarized, but variants are reported using polarized excitation.

A normal CD spectrometer cannot measure CPL, but a second hand CD spectrometer can be used as optical bench to measure CPL reversing the optics.

Fluorescence Detected Circular Dichroism (FD CD)

FD CD is the difference in fluorescence intensity for left and right circularly polarized light excitation.

Sample must be chiral.

$$\Delta F = F_L - F_R$$

Where F_L and F_R are fluorescence intensities with left and right circularly polarized excitation.

$S_F = \Delta F / \frac{1}{2} (F_L + F_R)$ or sometime you find $= \Delta F / (F_L + F_R)$

Since fluorescence is emitted in any direction it's a common practice to collect it placing PM tube at 90°, but in line measurements are possible with suitable filters, so:

FD CD can be measured with a normal CD instrument with very minor modifications.

Fluorescence Polarization

This originates from the fact that radiation emitted by a fluorophore may be linearly polarized.

$$P = (I_{||} - I_{\perp}) / (I_{||} + I_{\perp}) = \text{polarization}$$

$$r = (I_{||} - I_{\perp}) / (I_{||} + 2 I_{\perp}) = \text{anisotropy}$$

Sample is usually not chiral.

A CD spectrometer can measure FP only when equipped with LD accessory and other modifications.

Linear Birefringence (LB)

LB is the difference in *refraction* of linearly polarized light with normal planes of polarization.

$$LB = 2\pi l (n_{\parallel} - n_{\perp})/\lambda$$

A CD spectrometer must be equipped with a linear polarizer (after the sample) to measure a quantity related to linear birefringence.

Linear Dichroism (LD)

LD is the difference in *absorption* (or *emission*) of two linearly polarized beams with normal planes of polarization.

$$\Delta A = A_{\parallel} - A_{\perp}$$

Sample may not be chiral.

The CD spectrometer must be equipped with dedicated accessory (various types available)

Magnetic CB, CD, LB, LD

Applying a magnetic field parallel to incident light you can measure the *magnetic* components of above mentioned phenomena (i.e. induced by the magnetic field). MCB is the Faraday effect discovered more than 100 years ago.

MCB and MCD may be measured also on samples with no chirality.