

Optical Rotatory Dispersion Accessory for Chirascan (ORD.3)

Introduction

Optical rotation is the rotation of linearly polarised light as a result of passing through an optically active material and is a consequence of a difference in refractive index for the left and right circularly polarized light components (linearly polarised light can be written as an equal combination of right and left circularly polarised light). Measurement of optical rotation (i.e. at a single wavelength) is used in the characterisation and quantification of chiral molecules in research and industry.

Comparison of ORD and CD

The variation in optical rotation with wavelength is called optical rotatory dispersion (ORD). ORD spectra and CD spectra both derive from the interaction of polarised (circular or linear) light with chiral molecules and are directly related – as one can be derived from the other using Kramers-Kronig transform.

Measurements of ORD and CD can give essentially the same information, but experimentally one technique has been favoured for particular applications. CD is a higher resolution method since it is only observed for wavelengths where the chiral molecule absorbs light. This makes complicated spectra involving multiple absorption bands easier to interpret. Alternatively ORD measurements can be obtained at wavelengths where the chiral molecule being measured does not necessarily absorb light. This means that ORD measurements can be made on materials with high concentrations or where absorption bands are obscured by solvent or buffer salt absorption. The relationship between absorbance, CD and ORD is illustrated in figure 1.

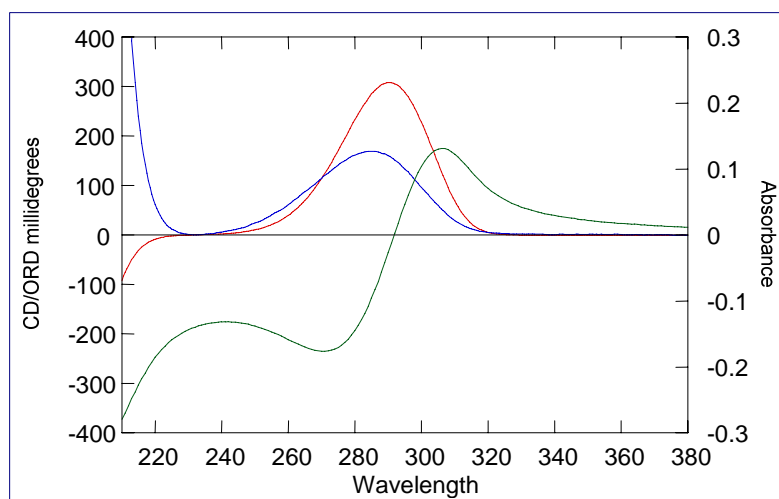


Figure 1 Overlaid spectra of Absorbance (blue), CD (red) and ORD (green) of the same solution of (1S)-(+)-10-camphorsulphonic acid (0.92 mg/mL in water in a 1cm cuvette) measured using the Chirascan and the ORD.3 accessory.

Principle of operation of chirascan with the ORD.3 accessory

The Chirascan ORD.3 accessory, shown in figure 2, adapts the Chirascan to measure ORD based on the method of Shindo *et al*^[1]. The accessory consists of a linearly polarising analyser prism on a rotatable mount and a dedicated detector. The photoelastic modulator (PEM) of the Chirascan is automatically configured by software as a dynamic half-waveplate, to output alternating vertical and horizontally polarised light. The analyser prism is placed after the sample and before the detector at a 45° angle (the null point) to the alternating vertical and horizontal light. When there is no optical rotation of incoming light the 45° linearly polarised component will have the same intensity for both the vertical and horizontal polarisations. If optical rotation does occur, then the intensity of the 45° component will alternate with the modulation of vertical and horizontal polarised light. The difference in signal can be obtained by using a lock in amplifier at twice the frequency (100kHz) of the PEM, and the detected AC/DC signal ratio used to calculate the rotation.

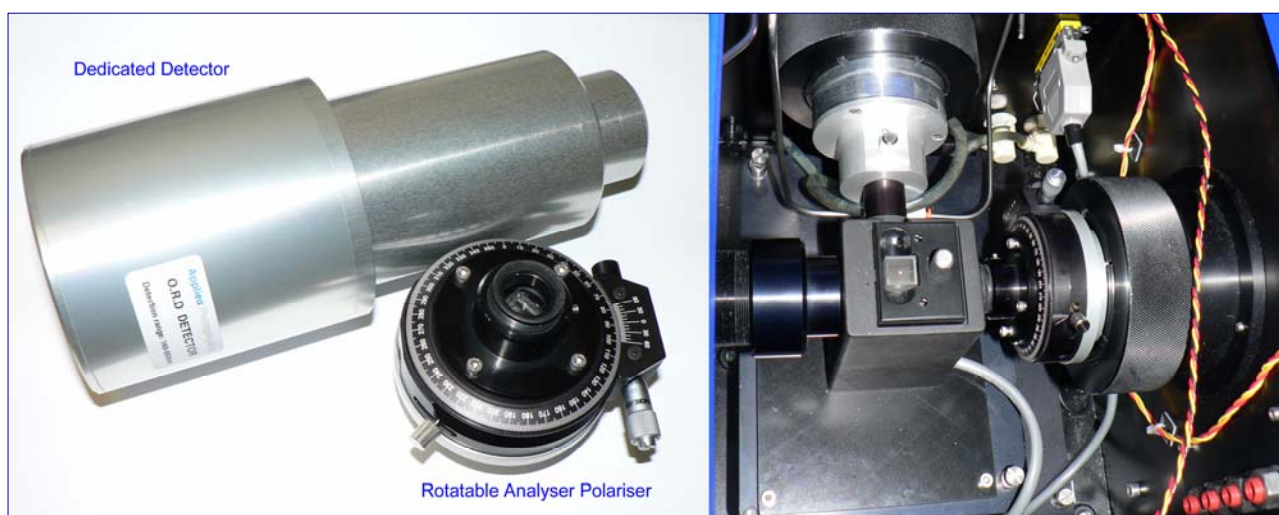


Figure 2 Left - The components of the ORD.3 accessory includes a dedicated detector and an analyser polariser on a precision rotatable mount. Right - the ORD.3 accessory installed in the sample chamber of the Chirascan.

Comparison between polarimeter and the chirascan ORD accessory

The Chirascan/ORD.3 system doesn't use the optical nulling method used by most commercial polarimeters, and so no physical rotation of an analysing polariser is required during data acquisition. The advantage of this approach for an ORD spectrophotometer is the ability to rapidly scan an ORD spectrum. Figure 3 shows a comparison of an ORD spectrum of a solution of sucrose (100mg/ml) compared to optical rotations from literature values at a number of single wavelengths^[2,3]. This ORD spectrum was collected from 300 to 700 nm with a 1nm data pitch in approximately 6.5 minutes, and higher scanning speeds are easily achievable.

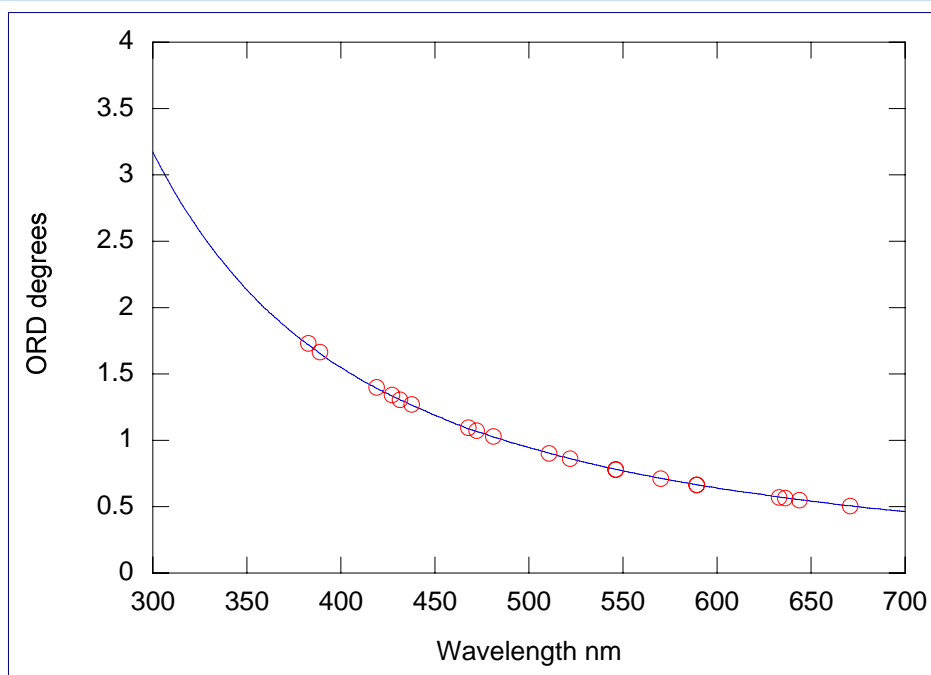


Figure 3 ORD spectrum of 100mg/mL solution of sucrose in water (1cm pathlength cuvette), recorded on a Chirascan fitted with the ORD.3 accessory (blue line) as well as literature values at a number of selected wavelengths^[2,3] are overlaid (red circles).

Conclusion

Although a more specialist area compared to CD, analysis of ORD spectra are useful in the analysis of chiral compounds and studies of absolute chirality that are complimentary to both CD techniques and single wavelength optical rotation measurements. The ORD.3 accessory extends the capability of the Chirascan to a fully capable fast scanning ORD spectropolarimeter.

References

- [1] Y. Shindo, H. Hayakawa, and M. Sudani, *Appl. Spectrosc.* 1989, **43**, pp. 1471-1475.
- [2] National Physics Laboratory, Kaye and Laby Table of Physical and Chemical Constants. Web Edition. 2007, www.kayelaby.npl.co.uk. Section 2.5.10.
- [3] T.M. Lowry, *Optical Rotary Power*, 1935, Longmans, Green and Co.