



## STRAY LIGHT IN CD SPECTROPOLARIMETERS

Burgess<sup>1</sup> defines stray-light (or stray radiant energy, from now on SRE) as 'radiant energy to which the detector is sensitive, and which should not be there'.

SRE is composed by wavelengths outside from the band nominally transmitted by the monochromator which reach the detector, every spectrometer, including your CD, will have a certain amount of SRE.

Effect of SRE in a UV-VIS spectrophotometer is to provide a greater than real transmittance.

Let us assume that at a specific wavelength SRE is 0.1%: if our sample at same wavelength should have 1% transmittance (2 OD), our spectrophotometer will measure 1.1%T or 1.958 OD, with a 2% error, if our sample has 3 OD (0.1%T) we will measure 0.2%T (2.699 OD) with an error of 10%!

Reasons why SRE is present and way to measure it are detailed in many books<sup>2,3</sup>, here we want only to remember that SRE is dependant from the wavelength.

In our CD spectropolarimeters SRE may be an important factor since units use very bright Xe lamps with strong emission in the visible region and relatively low emissivity in the far UV where spectra are often collected. The use of double monochromator substantially helps in reducing SRE.

We have seen potential effect of SRE in a spectrophotometer, what about in a CD spectropolarimeter? Systems use dynode feedback so the DC component is kept constant while only the AC one is measured by the lock-in amplifier. So assuming, as before, that the DC component is 1% of the incoming light (2 OD) and SRE at same wavelength is 0.1% our dynode feedback will operate with 1.1 times the expected light, depressing the CD signal measured by the lock-in amplifier by 10%. If absorbance is 3 OD (0.1%T) with same 0.1% of SRE the measured CD signal will be depressed by a flat 50%.

So SRE is more a serious concern in CD rather than in absorption spectroscopy.

Despite this fact stray light level is rarely reported in the commercial specifications, a few examples:

-Cary 60 (in 1969) less than 0.005% between 200 and 600 nm and less than 0.1% at the operating limits (185-600 nm)

-J.Y. Mark V (from a 1988 quotation) less than 0.005% at 185nm, no specs from more recent CD6 leaflet in my hands

-Jasco no specs from commercial leaflets up to current J-810 in which 0.0003% at 200nm is reported, a published detailed report<sup>4</sup> of 1994 indicates 0.00005% at 220nm using ASTM method<sup>5</sup>

-AVIV 62DS and current 202 less than 0.001% at 200nm

-Applied Photophysics  $\pi^*$  180 CDF, no specs found

-OLIS RSM less than 0.01% in the operating range

More important no trace is usually given on how SRE is measured. If you consider monochromators manufacturers they usually express SRE measured filling the system with a laser source and measuring SRE at a certain wavelength shift from the laser line ..... this is clearly a different method from what we require!

All these arguments do not take into account another couple of sources of mismeasurement:

-CD systems are single beam units with unchopped light. So DC level may be influenced by the dark current of the photomultiplier (not so young people will remember the "dark current" multipot of the Beckman DU!)

-saturation of the lock-in amplifier by noise may be another important limiting factor when high voltage is very high So how to take care? Keeping absorption of sample + solvent below 2 OD (ideally for best results below 1 OD) will keep us in the safe side, so when necessary use shorter path cells.

And in low UV, where oxygen absorption is the key factor ..... purging, purging well with dry nitrogen. Incomplete purging will be the major cause of SRE in low UV, much-much more significant than any other!

<sup>1</sup> Burgess C. *Encyclopaedia of Analytical Science*, Academic Press, Adam Hilger, (1995), 3643-3647

<sup>2</sup> Burgess C., Frost T. *Standards and Best Practice in Absorption Spectrometry*, Blackwell Science (1999)

<sup>3</sup> Castiglioni E. *Spettrofotometria UV-VIS Criteri di Valutazione e Controllo*, Morgan Edizioni Tecniche (1996)

<sup>4</sup> Jasco Technical Information AW-037/TI94 (1994)

<sup>5</sup> ASTM standard E-387 (*Annual Book of ASTM Standards*) (1984)