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POLARIMETRIC ERRORS

The only sure way to *calibrate* the vertical scale of a CD spectrometer is to use an accepted standard, of known concentration, certified optical purity and accepted $[\alpha]_D$.
This means that *we do need a polarimetric measurement*.
Conventional polarimeters are optical-null type, so their built in accuracy is by definition limited only by the quality of the gears which rotate the analyzer: due to high reduction rate, expected needs should be easily matched.
Even an aged system will measure accurately ……., age and deterioration will increase the noise and so decrease the precision, but not the accuracy.
Polarimetric calibration can be checked with suitable standards, such as NIST (National Institute of Standards & Technology, Gaithersburg, MD 20899) SRM 17e Sucrose or with *quartz plates* supplied by different manufacturers with NIST traceability.

Unfortunately you may discover that even your supposedly accurate polarimeter provides an $[\alpha]_D^{20^\circ}$ not perfectly matching the expected NIST result, (66.524 ± 0.054 for Sucrose), how is it possible?

Let's assume we are preparing perfect solution following NIST procedures, with proper skill and accurate tools, still:
- first of all the temperature. It may be difficult to compensate effectively temperature, small changes are significative (problem is here even when we deal with quartz plate standards, pls ask detailed information to your supplier).
  Ambient temperature monitoring will give little help, since temperature in the sample compartment is usually higher
- some polarimeters may somehow vignette the measuring beam using micro cells. Be sure to use standard ones with large aperture, not intercepting the light beam.
- measuring wavelength may not be correct:
  a. for units with spectral lamp (typically Na), there is an interference filter to cut off spurious lines emitted from the source (any Na lamp has also Hg inside). If filtering is not effective the 577nm of Hg may pass through too: this will increase our readout.
  b. For units with halogen lamp and filter the error is built in since:
     I - central wavelength of filter may be not the required 589.44 nm
     II - since sucrose reading increase toward the UV not in a linear way, a bandpass filter, even if perfectly centered, will overestimate readings
     III - a mirror collimates beam from light source. Source is not punctual, so beam through the filter will not be perfectly parallel. This will somehow shift toward the UV the central wavelength
     These factors together may induce a sizeable error, it's calculated that 1 nm mismatch will induce an overestimate of about 0.375%

From the above considerations you must be critical in judging results, even for a supposed *sure and reliable* technique as polarimetry.
While overall error may be small[1], we shouldn't forget it, since our standards for CD will be measured with the same unit!

[1] it's now a common practice to use *validation* software or protocols to check polarimeters performance. However these too will hardly give any benefit (apart from the formal aspect) since the source of error listed above are not considered.

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