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AN EDUCATIONAL CD SPECTROMETER

At 14th International Symposium on Chirality (ISCD14, Hamburg Sept 8-12, 2002) the enclosed poster was presented.
Nothing really new, but you may find some interest in it.

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A new low cost Circular Dichroism spectrometer for educational purposes

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CD instruments in the past

Circular Dichroism was measured in different ways, for example:

G.M. Holzwarth in his famous paper of 1965 on the CD of polypeptides[1] was using a Beckman DK-2A adapted in two different ways:
-using a quartz polarizing prism and a quartz retardation plate in the sample beam of the spectrophotometer.
-using an electro-optical modulator (Pockel cell) as in *modern* units
Details on the first approach were published separately[2], spectra were measured interpolating the points at which the plate is giving $\lambda/4$ retardation.

Shimadzu[3] in the late sixties produced two CD accessory for its manual single beam spectrophotometer QV-50. Both accessories (QV-13-00 and VCD-1) were using a prism linear polarizer to generate linearly polarized light followed by a Babinet-Soleil compensator to get circular polarization before the sample.

Fica[4] was converting their ORD spectrometer (based on dual Faraday cell compensation) to CD measurement simply inserting a Fresnel rhomb in the path.

Applied Physics Corporation in 1966 presented at Pittcon a CD accessory for their Cary 14 double beam spectrophotometer. The accessory[5] was based on quartz polarizer – Fresnel rhomb assemblies placed in sample and reference compartment of the unit.

Abu-Shumays & Daffield article on Analytical Chemistry[6] reports different ways to measure CD from early times.

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1 Holzwarth G., Doty. P., *J.Am. Chem.Soc.*, 87, 1965, 218
2 Holzwarth G.M., *Rev. Sci. Instr.*, 36, 1965, 59
3 Shimadzu Seisakusho Ltd, *QV-50 brochure*, ~ 1968
4 FICA, *Spectropol 1 brochure*, ~ 1967
5 Cary Instruments, *Technical Report Mod. 1401 CD Accessory*, 1966
6 Abu-Shumays A., Duffield J.J., *Anal. Chem.*, 38, 1966, 29A

CD instruments today

All commercial CD instruments today are based on the Grosjean & Legrand method[1]*:

> *monochromatic light is linearly polarized, than it pass through an electro optical modulator where the polarization is modulated at the modulator frequency alternating between left and right circular polarization. If sample is CD active the detector output signal will contain an alternating component V_{ac} and a continuous component V_{dc}. Ratio between V_{ac} and V_{dc} is the CD effect we want to measure. A non CD active sample will have $V_{ac}= 0$, while the phase of the AC component will indicate the polarity of the phenomena.*

In normal operation V_{dc} is kept constant by dynode feedback, so only V_{ac} is measured.
Since than the real improvement has been passing from the original modulators based on fragile Pockel cells to the currently used photoelastic modulators (PEM)[2], in which linear birefringence is induced on a quartz plate (for UV-VIS range) by mechanical stress.
The higher frequency of PEMs (several KHz) allows to use sensitive phase detection lock-in electronics, widely improving sensitivity and stability.
Drawbacks of PEM (as in old Pockel cells) are the need of programmed drive to provide exact1/4 delay, the high cost, and potential double frequency artifacts, which will be evident when dealing with oriented samples …..

** this is actually not correct: CD instruments made by OLIS use a variant of the method: light at monochromator output is linearly polarized, but both polarization components passes through the PEM and the sample to reach two separate PM tubes. Log of the ratio of the two detectors output (called by them DSM – digital subtraction method) will provide the DC signal. Approach is advertised for its higher sensitivity, since both linear polarizations are used, but there are many drawbacks behind not to be discussed here.*

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[1] Grosjean M., Legrand M., *Compt. rend.*, 2651, 1960, 2150
[2] Kemp J.C., *J. Opt. Sci. Amer.*, 59, 1969, 950

Other CD applications

With the term CD spectrometer we normally refer to units working in the UV-VIS range (so called ECD units), but this is somehow too simple today:

-far UV CD
are the units working typically with synchrotron light, measuring approach is similar to ECD units.

-NIR CD
typically based on either grating monochromator design (in this case similar to ECD units, but with the need to measure also V_{dc}, since dynode feedback is not possible) or on FT/interferometer, which for same consideration as for VCD will apply.

-VCD
CD spectrometers for IR range are based either on dispersive grating mounts (typically home-made) or on FT/interferometers (available also commercially).
A PEM with proper wavenumber coverage is used here (normally ZnSe). Measuring technique is more complex since in addition to the PEM light modulation you have the one coming from the interferometer moving mirror (or from the chopper of the dispersive unit). So to extract CD information you must still measure V_{ac} and V_{dc}, butt both are further modulated. In addition proper ¼ wave delay can be assumed true either in a limited wavenumber range or you are compelled to not so easy compensations.
So far only a few units not using a PEM have been assembled[1] [2].

If we move furthermore to other related techniques such as CPL or ROA we will still find wide use of PEMs, until they can match the frequency response of the detecting systems.

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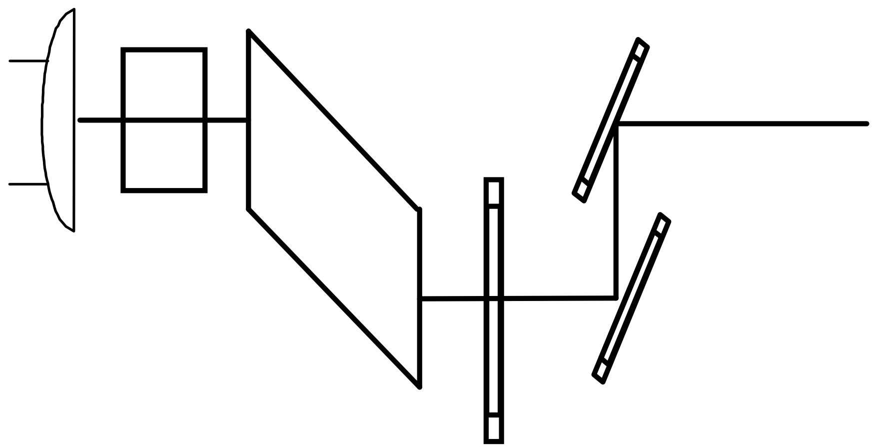
[1] Malon P., Keiderling T.A., *Appl.Spectrosc.*, 50, 1996, 669
[2] Azzam R..M.A., *Opt.Lett.*, 2, 1978, 148

Our approach

The idea was to arrange an accessory fitting the sample compartment of a commercial UV-VIS spectrophotometer.
We selected the lower cost double beam model of Jasco (V-530, selling price in Europe about 6000 €).

Basic specs are:
-concave grating monochromator
-D_2 and halogen source
-2nm fixed bandpass
-Si diode detectors (one for each beam)
-removable sample compartment
-PC control and data processing



We arranged a new sample compartment including:
-two flat mirrors to deflect the sample beam
 (15x15mm from SUWTECH)
-one linear polarizer
 (105UV from Sterling Optics)
-one UV grade fused silica Fresnel rhomb
 (FRP1104 from SUWTECH)

Path in the reference beam side was left empty*

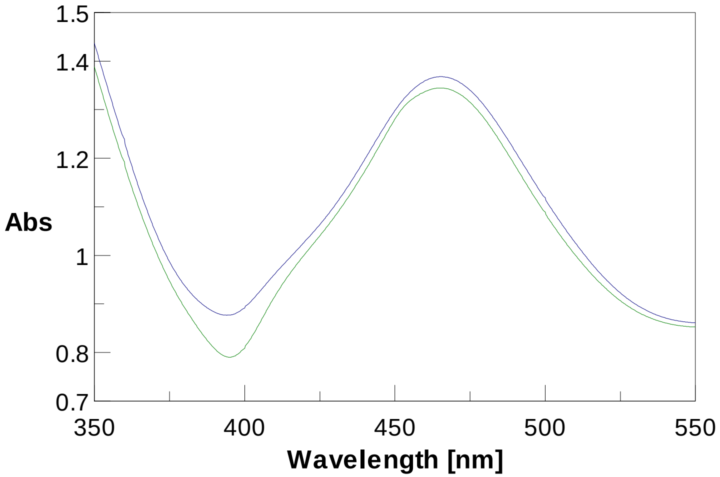
**We also tested double beam approach using same layout in both beams with relatively crossed polarizers, this works as well, but it's more complex.*

Way to measure

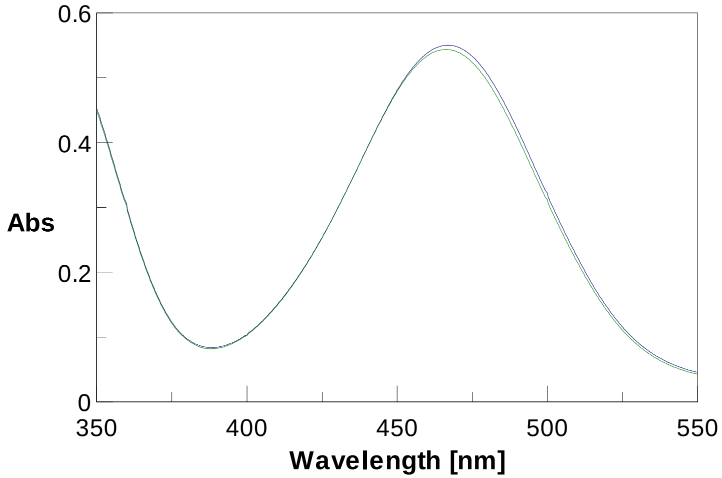
Measuring approach is very simple:
You collect sample and blank spectra in absorbance scale with polarizer in one position and subtract the data.
Than you rotate polarizer 90° and repeat procedure.
Finally you subtract the two files to get your CD spectra.

To test the system we used a typical CD standard ; a water solution of 2(+)$_D$-[Coen$_3$]Cl$_3$·NaCl·6H$_2$O in a 1cm path cell.

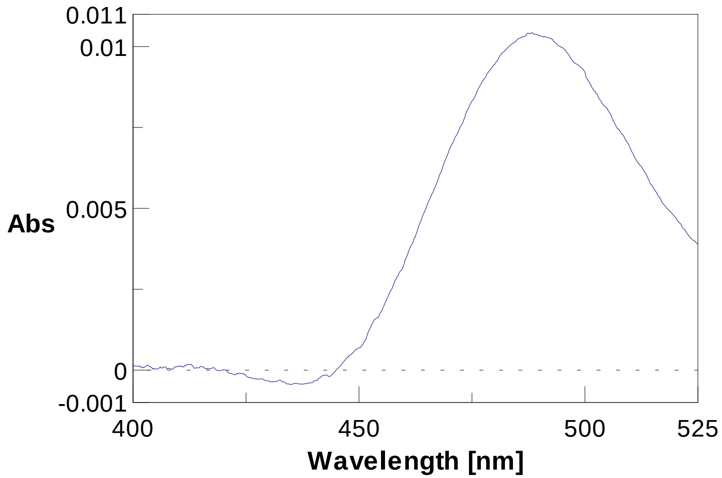
Figure below is showing the overlay of the two spectra for each individual polarizer orientation without baseline correction, this shows how baseline correction is important.



Next figure shows baseline corrected spectra



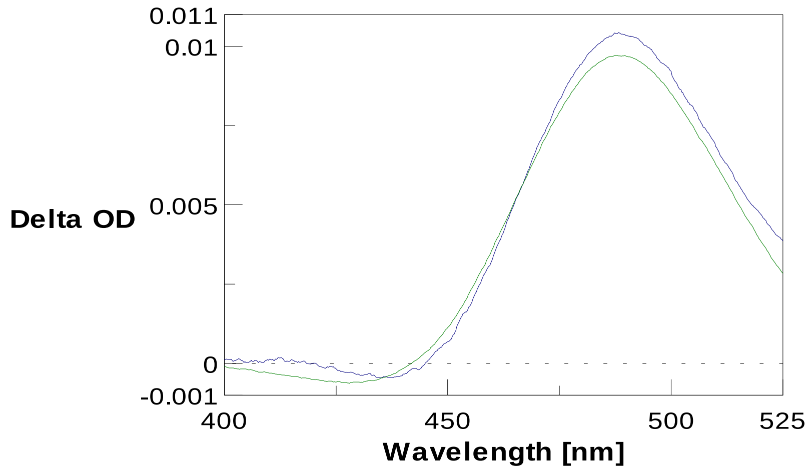
Last one shows the calculated CD spectra



Limitations

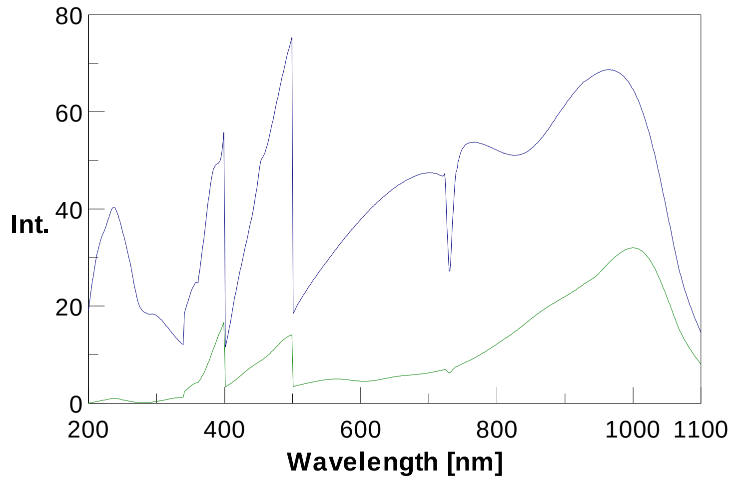
Apart from the relatively long/multi-step measuring procedure, quality of results is limited by many factors. First of all V-530 uses a rather weak light source and insensitive detection system compared to a conventional CD instrument.

The picture shows same spectra as obtained with a Standard CD instrument.
S/N is at least one order of magnitude lower, so the approach is limited to samples with rather high g factor.
Moreover spectral distortion are present, caused probably by the poor system to rotate the polarizer and by quality of polarizer itself and Fresnel prism.
Last, but important light beam path is focused in the center of the compartment, so beam is not parallel through the Fresnel rhomb.



But other limitations are coming from the hardware used.

Figure shows single beam *energy* spectra of our V-530
With empty sample compartment and with the device fitted:
-data above 750nm has no meaning since polarizer is not working in NIR
-apart from gain changes at 500 and 400nm (part of the V-530 design) strong and weak Wood's anomalies are present due to grating monochromator. These are very dangerous since highly sensitive to linear polarization.
-efficiency drops significantly in the UV due to the selected components



Conclusion

Given the fact that experiment was not designed to foresee any future commercial application, we think that it has two main benefits:

-educational
the layout is very simple and the cost of components is very small. It'd be easy to duplicate the arrangement in any laboratory interested in teaching the CD technique and its basic fundamentals.
No modification at all is necessary on the spectrophotometer you'll use.
Putting sample after the polarizer and before the Fresnel you can additionally measure LD (linear dichroism).

-research
this old static approach may deserve some attention also for special instruments.
Since we have no PEM and no dynamic polarization modulation, same approach may be adopted to build a VCD based on a conventional FT/IR spectrometer, here too without any modification in the detection electronics and data processing.
Our next step will be exactly in this direction: using a ZnSe Fresnel rhomb and a manual or automated: wire-grid polarizer on a conventional FT/IR we plan to arrange a VCD instrument.
Here too we will be less sensitive than commercial VCD equipment's based on PEM modulators, but we will greatly benefit not having multiple modulation to sort out how to extract the CD signal. We should further benefit from a wider wavenumber range and chromatic influence of quarter wave retarder is another plus.
Moreover, in contrast with what presented here, we will use same sort of source and detector used in commercial VCD, without any loss in *energy*.