

OLIS Circularly Polarized Luminescence Spectrophotometers

Technologically superior, smaller, and less expensive
than choices from Jasco, Applied Photophysics, and Edinburgh Instruments

At the encouragement of Muller, Riehl, and others in the early 2000s, On-Line Instrument Systems (OLIS), Inc. added circularly polarized luminescence spectrometers to our product line.

Our approach was to develop a novel sample compartment which allowed positioning of the polarization hardware before the sample for CD and after the sample for CPL. This 'Polarization Toolbox' accommodates both polarized measurement light (CD) and polarized emitted light (CPL) with no hardware additions.

A third model was developed in 2019 for CPL only. This emission-only model has none of the large and expensive hardware required for circular dichroism. Exactly and only the hardware required for highest sensitivity CPL is used, resulting in a physically small and very affordable circularly polarized luminescence spectrometer, the OLIS CPL Solo.

Polarization Toolbox

This sample compartment was developed to eliminate any redundancy of hardware for CD and CPL measurements. Instead of duplicating hardware, one positions the polarizers and the photoelastic modulator (1) before the sample, (2) after the sample, or (3) out of the optical train.

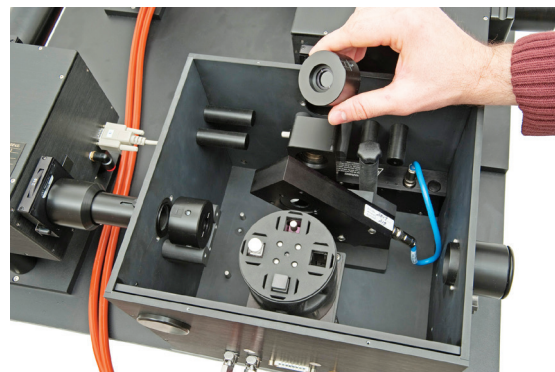
This open-architecture design eliminates the cost and redundancy of two photoelastic modulators, as is used in the Jasco and Applied Photophysics CPL systems (read more on this ahead).

The Polarization Toolbox is also an excellent pedagogical resource. With one instrument, one can move among absorbance, fluorescence, polarization of fluorescence, circular dichroism, and circularly polarized luminescence simply by adding or repositioning the polarization pieces. The repositioning of the polarizer(s) and PEM requires no tools, optical alignment, calibration, or other process. It is easy and quick.

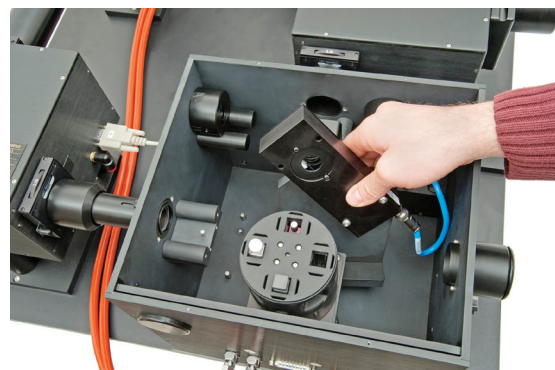
(However, should you prefer to purchase two PEMs so as to avoid repositioning one between CD and CPL measurements, you are free to do so.)

The photographs (at right) show the interior of the Polarization Toolbox with its lid removed. Here we see an optional four position cell holder. CPL experiments can be very lengthy, so controlled temperature(s) can be quite desirable. This four position Peltier holder allows one to do up to four experiments without user intervention.

Choose a single or 4-position Peltier for computerized temperature control, so as to hold a sample at a given temperature over hours of data collection or to vary temperature for a thermal melt or other temperature dependent study.



Moving the polarizer



Moving the PEM

Optimize for Sensitivity (CPL) or Stray Light (CD)?

Circularly polarized luminescence (CPL) demands highest sensitivity. Thus, the ideal instrument has minimal optical surfaces (mirrors and gratings) as well as the highest intensity light sources.

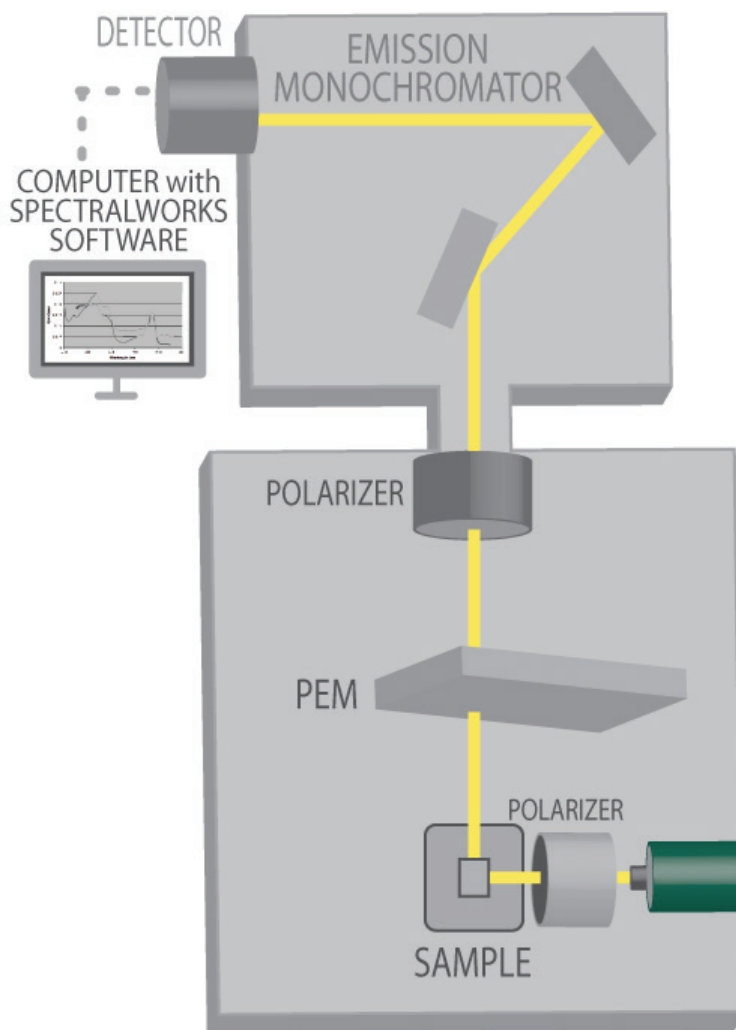
On the other hand, **circular dichroism (CD)** demands very low stray light, which is achieved using a double monochromator plus the high intensity light source.

The two OLIS instruments that support both CD and CPL therefore include a double monochromator. These double monochromators required for CD produce the excitation light for CPL.

The **OLIS DM 245** uses the small Hummingbird subtractive double grating monochromator with a spectral range of 170-700 nm or 200-900 nm. As a “subtractive” double, this monochromator creates a homogeneous output beam, independent of the spectral bandpass. An ‘additive’ double monochromator produces a heterogeneous output beam, so that wavelengths within a bandpass are spatially separated.

The **OLIS DSM 172** uses the classic Cary 14/17 prism-grating additive monochromator with spectral range of 185-2600 nm, making it the ideal choice for laboratories working in the NIR region.

Our model which does not support CD – the **OLIS CPL Solo** – has no large, expensive double monochromator because it is optimized expressly for sensitivity. Compare this with the Jasco CPL-only model – the CPL-300 – which has TWO double monochromators, yet ironically, does not support CD acquisition.



The fewer optics the excitation passes through, the higher the sensitivity. Thus, on a model from which CD is not expected, a laser or a (filtered) LED is used for highest intensity excitation light.

The elimination of large and expensive CD-specific hardware with low cost, high intensity LEDs is what allows us to create the low priced CPL Solo.

Detecting CPL: Optimizing for Sensitivity

For all OLIS CPLs, a gated photon counting PMT is used. These digital detectors have 20x higher sensitivity than the analog photomultiplier tubes used in all commercial CD spectrometers.

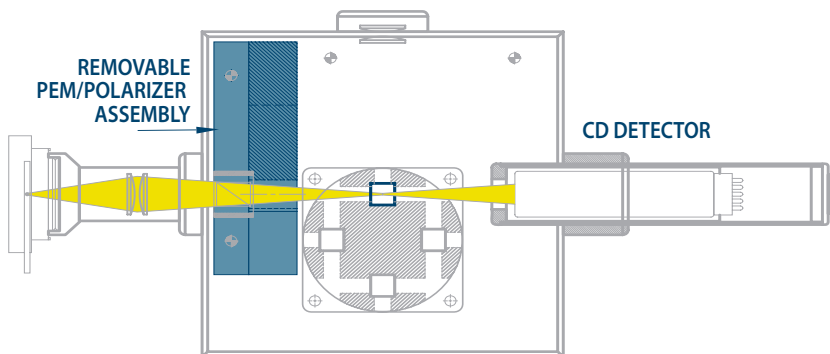
The active spectral range of this photon counter is 230-870 nm. At much higher price, NIR photon counters are available, too.

Only OLIS models collect directly, absolutely, and entirely digitally

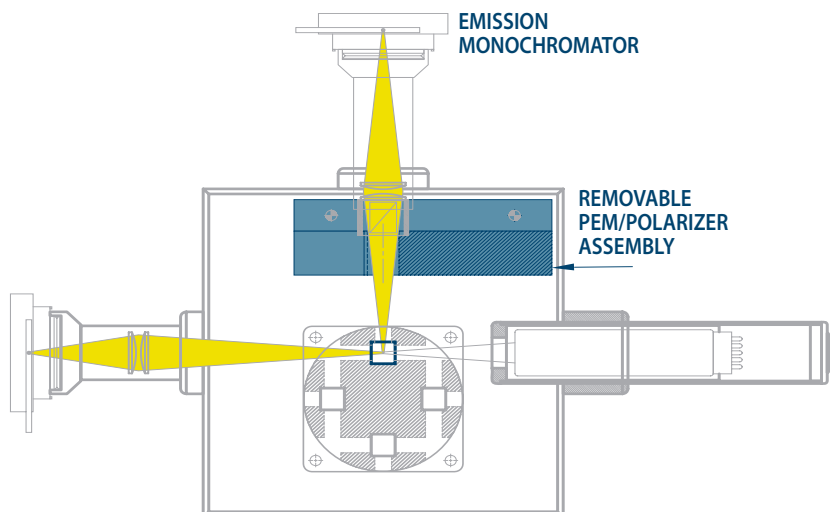
OLIS software employs an entirely digital data collection scheme, eliminating the use of 1960s era lock-in amplifiers and associated settings to decouple and modify the raw signal before it reaches the detector. This entirely digital method eliminates 100% concern about calibration, G-factors, and incorrect user settings.

OLIS software tags every raw datum of the 500,000 collected per second for time, wavelength, and state of polarization. Originating from the raw data and modified only mathematically, the resulting digitally acquired answer can only be perfect.

- For CD, the digital OLIS method is exactly $\text{abs(L)} - \text{abs(R)} = \text{CD}$
No calibration factor is required for CD
- For CPL, the digital OLIS method is exactly $\text{fluo(L)} - \text{fluo(R)} = \text{CPL}$
No G-factor is required for CPL



OLIS DM 245 in CD MODE
PEM is between incoming light and the sample, creating polarized measurement light.



OLIS DM 245 in CPL MODE
PEM is between the sample and the emission monochromator, analyzing polarized emitted light.

Addressing information published by Jasco, Applied Photophysics, and Edinburgh Instruments:

Jasco Statement: "The standard ozone-free 150W Xe arc lamp can be replaced with an Hg/Xe source."

OLIS Response:

We see no justification or explanation for a mercury lamp. Obviously, one could be used, but to what end?

Jasco Statement: "The instrument's unique double-prism excitation and emission monochromators offer very low stray-light and no spurious linear polarization effects caused by instruments that use diffraction gratings. These are both extremely important as CPL signals tend to be very weak."

OLIS Response:

1. "Linear polarization effects caused by instruments that use diffraction gratings" is not a concern in the CPL Solo, since it has no optics on the excitation side. Thus, there is no linear polarization being caused. Measuring for LD is easy on the scanning models, allowing you to decide whether the addition of a depolarizer is worthwhile.
2. Stray light is not a parameter of interest in CPL. High sensitivity is always the higher priority.
3. Yes, "CPL signals tend to be very weak." The way to address that is the **exact opposite of what Jasco offers.**

Jasco Statement: "Double-prism monochromator"

OLIS Response:

1. As noted previously, our subtractive double grating monochromator on the OLIS DSM 245 does have meaningful advantage of a homogeneous output beam independent of the bandwidth and zero temporal dispersion. And, our Cary prism-grating monochromator used in the OLIS DSM 172 has the meaningful advantage of the vast 185-2600 nm useful range. A double monochromator is required for CD; it is of negative consequence for CPL.
2. The Jasco CPL-300 uses TWO large, expensive, light absorbing double prism monochromators, detrimental to sensitivity, filling a 2 meter length, and costing over \$200,000.



The Jasco CPL-300 uses two Jasco CD spectrometers linked to create a CPL system nearly 2 meters long and ironically incapable of CD.

Jasco Statement: "180° sample geometry with unpolarized excitation light"

OLIS Response:

1. There is no advantage to this "feature."
2. Any model can have unpolarized excitation light with the addition of a depolarizer.
3. LEDs – as are used in the CPL Solo and as are recommended for use with the OLIS DSM 172 and 245 – produce unpolarized excitation light.

Jasco Statement: "Excitation (Ex) and emission (Em) monochromators"

OLIS RESPONSE:

All CPL spectrometers have monochromators on both the excitation and emission sides, other than the CPL Solo, which has wavelength specific LEDs on the excitation side for higher sensitivity, smaller footprint, and lower cost.

Jasco Statement: “Low stray light, no second-order radiation and no Wood’s anomalies”

OLIS RESPONSE:

1. There is zero value in “*low stray light*” in CPL. As an example of how irrelevant stray light is, refer to this chart produced by another supplier (Applied Photophysics) showing a “33 nm” excitation bandpass:

Setting	Value
Excitation Wavelength	373 nm
Excitation Bandwidth	33 nm
Emission Range	570-630 nm
Emission Bandwidth	3 nm

If an additive double monochromator is used with a 33 nm bandpass, the sample will receive this light as a spatially distinct rainbow of wavelengths, each wavelength striking a distinct part of the sample. With the subtractive double monochromator, the 33 nm are blended into a homogeneous beam, so that the sample is excited with a single blended color.

2. The concern about “*second-order radiation*” is spurious.
3. The concern about “*Wood’s anomalies*” is spurious.

Jasco Statement: “Samples with different transition moments for absorption and fluorescence, that do not become depolarized, can be measured”

OLIS Response:

This is a nonsensical statement.

Jasco Statement: “Selectable Ex wavelength and Em spectral bandwidth”

OLIS RESPONSE:

All commercial CPL models have selectable excitation and emission spectral bandwidth.

Jasco Statement: “High-throughput optical system and highly sensitive PMT ”

OLIS RESPONSE:

1. The lengthy optical train of the Jasco CPL-300 produces the opposite of “*high-throughput.*” It is highly absorbing and thus has lower light throughput than a smaller and shorter optical train.
2. Also, “*highly sensitive PMT*” is not the exquisitely sensitive gated photon counter that is used in all OLIS CPL spectrometers (and potentially by others).

Jasco Statement: “Increased fluorescence sensitivity”

OLIS RESPONSE:

There is no explanation for or proof of this claim

Jasco Statement: “Data collection and processing”

OLIS RESPONSE:

One hopes!

Jasco Statement: “Simultaneous measurements of CPL and fluorescence intensity”

OLIS RESPONSE:

This will be true for all CPL spectrometers.

Jasco Statement: “One-click data conversion to DI and G_{LUM} ”

OLIS RESPONSE:

While this statement is made, all data shown by the Jasco CPL is displayed as millidegrees, units which are meaningless for CPL. Can a CD value be converted to G_{LUM} ?

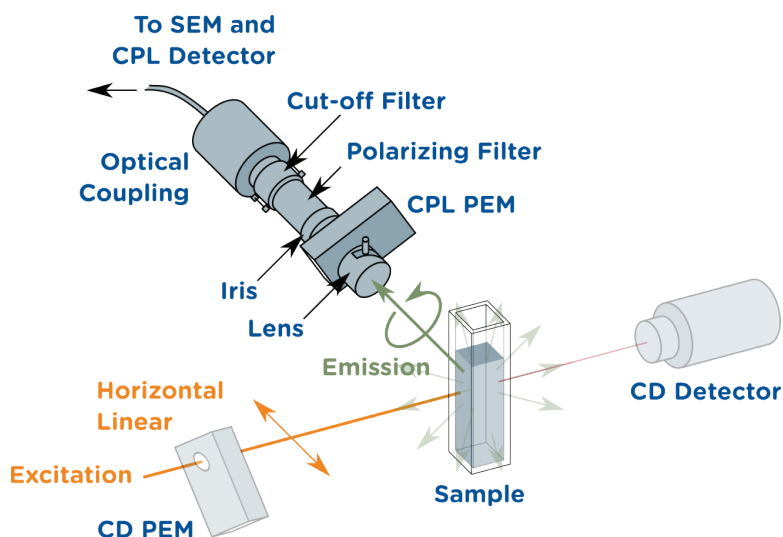
Retail List Price for US customers (December 2019):

CPL ONLY:

Jasco CPL-300: over \$200,000

OLIS CPL Solo: under \$100,000

Applied Photophysics' CPL addition to their Chirascan CD:



This graphic from their site shows that two PEMs are used, one for CD and a second for CPL. OLIS can offer the same, but our default recommendation is to move one PEM between measurements to save money and eliminate redundancy.

Applied Photophysics Statement: "In addition to CPL data, CD and absorbance data was [sic] obtained without changing the experimental setup."

OLIS Response:

If one wants to purchase the emission channel PEM for similar hands-free transition between CD and CPL on an OLIS, he can; however, the 2-3 minute tool-free movement of the PEM from the CD channel to the CPL channel is standard.

Applied Photophysics Statement: "The Chirascan CPL accessory enables comprehensive analysis of chiral luminophores and is compatible with CD measurements."

OLIS Response:

Two OLIS models support CD and CPL. The CPL Solo measures CPL only and can be very much smaller and far less expensive than the models which support both.

Applied Photophysics Statement: "CPL and CD measurements with the same instrument setup and sample"

OLIS Response:

While it is entirely possible to do CPL and CD on identical samples, this will be an infrequent situation in most laboratories. Exactly as one produces a sample in a buffer and concentration optimized for absorbance or fluorescence, one should do this for CD or CPL, which are far smaller and thus more challenging signals to acquire than their non-polarized forms.

Applied Photophysics Statement: "Multiple ways for optimizing light throughput"

OLIS Response:

There is no explanation for or proof of this claim.

Applied Photophysics Statement: "Full software integration for easy acquisition of both CD and CPL measurements"

OLIS Response:

One would hope so!

Retail List Price for US customers (December 2019):

CPL and CD:

Applied Photophysics: over \$150,000

OLIS DSM 172: under \$150,000

OLIS DM 245: under \$150,000

Edinburgh Instruments' addition to their FLS1000 (or FLS980)

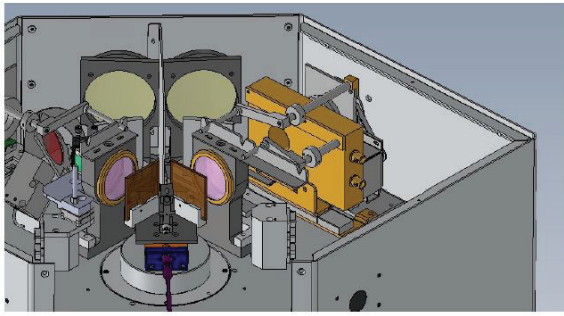


Figure 1: CPL System Sample Chamber (PEM in yellow).

This company offers to add a PEM, lock-in amplifier, and software to a large and expensive spectrofluorimeter. One must purchase or own the fluorimeter to do CPL on an Edinburgh.

Edinburgh Instruments Statement: "Circularly polarized luminescence (CPL) measurements can be made on an FLS980 spectrometer which has been modified to include a photo-elastic modulator (PEM) and lock-in amplifier CB1 box."

OLIS Response:

This makes perfect sense: add the required additional hardware to a high quality spectrofluorimeter. Presumably, homemade CPL instruments have taken this form, too.

Edinburgh Instruments Statement: "The FLS980 comes standard with a 450 W ozone free xenon arc lamp that covers a range of 230 nm to 1000 nm for steady state measurements."

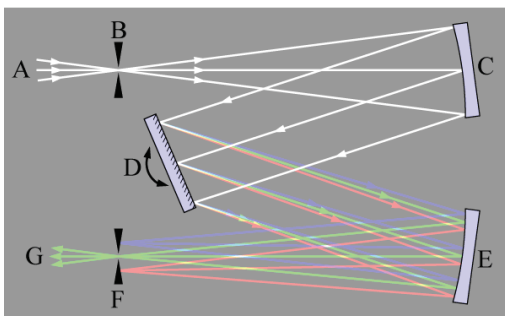
OLIS Response:

A 450 watt xenon arc lamp is exceedingly noisy, so that there will be tremendous variation in excitation intensity among wavelengths and from one measurement to the next. But, there will be a lot of light!

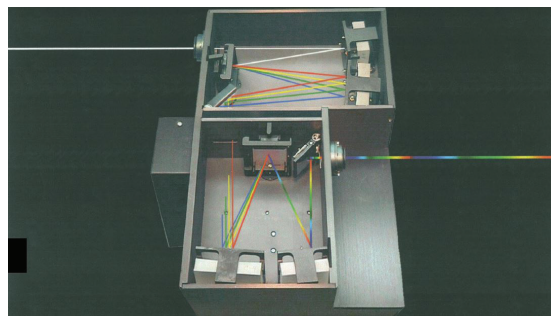
Edinburgh Instruments Statement: "Single and double grating Czerny-Turner monochromators are available in the FLS980"

OLIS Response:

This graphic of a Czery-Turner monochromator (found on Wikipedia) well illustrates the nature of all additive double monochromators: the output beam (the light that reaches the sample) is spatially dispersed, so that different parts of a sample see different wavelengths. Compared this with the light from a subtractive double monochromator – such as on the OLIS DSM 245 – which is homogeneous, so that the sample sees a perfect blend of the wavelengths reaching it.



Czerny-Turner monochromator



Subtractive double monochromator

Edinburgh Instruments Statement: "The instrument comes standard with a R928P PMT detector in a cooled housing which covers a range from 200 nm – 870 nm."

OLIS Response:

One presumes this detector is used in its photon counting mode.

Retail List Price for US customers (December 2019):

CPL ONLY:

Edinburgh Instruments: over \$125,000 OLIS CPL Solo: under \$100,000