

Measuring Sea Water Color Dissolved Organic Matter (CDOM) in Real Time with Liquid Waveguide Capillary Cell (LWCC)

CDOM detection

Dissolved organic matter (DOM) forms the largest reservoir of reduced organic carbon in the ocean. Measurement of DOM light absorption is one method to describe the biogeochemistry and hydrography of different oceanic regions and water masses. CDOM (Colored Dissolved Organic Matter) is a part of the DOM pool and can be determined by optical methods, notable absorbance measurements using LWCC long-path flow cells. CDOM concentration depends on the location where samples were taken, with coastal waters showing higher CDOM concentrations compared to open-ocean waters (e.g. Figure 1). In addition, CDOM absorption depends on open-ocean water depth. Literature based corrections are proposed to consider baseline offsets due to salinity and temperature. Traditionally, CDOM samples can be obtained by filtering the fresh or sea water sample with a 0.2 μm vacuum filter system.

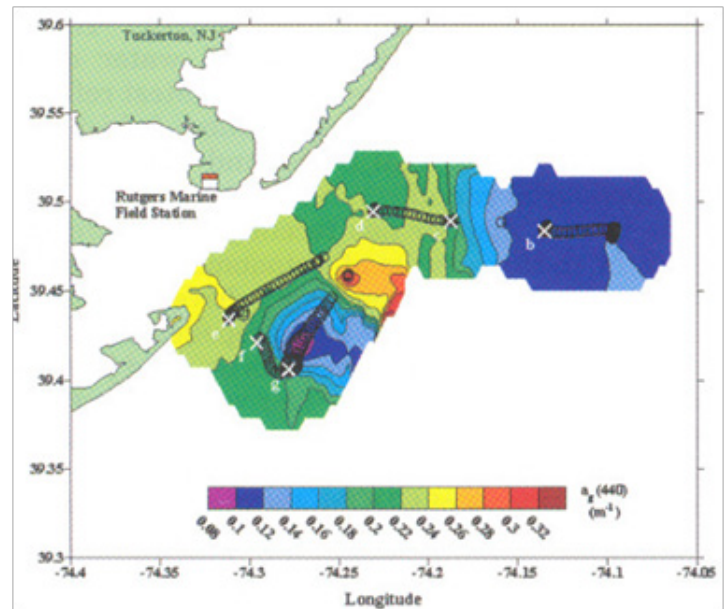


Figure 1. Graphical representation of geographical dependent variations in CDOM concentration. Color scale for CDOM absorption at 440nm. Reprinted/adapted with permission from Kirkpatrick GJ et al. *Applied Optics* 42, 6564 (2003), The Optical Society.

Common applications of CDOM detection

- Role in biogeochemical cycles, e.g., the organic carbon-based cycle in the ocean
- Role as a tracer substance for monitoring and mapping of surface-water masses, i.e., hydrography
- Regulation of UV light penetration into the ocean
 - Role in ocean photosynthesis reaction with effects on phytoplankton population
 - Oceanic food chains
 - Primary source of atmospheric oxygen
- Light absorption of CDOM as part of heat storage with effects on the decline of sea ice



LWCC FOR CDOM MEASURING

Advantages of LWCC measurement

- Improved dynamic range for a broader range of absorbance measurements
- Improved sensitivity of the measurement so you can detect lower concentrations of solutes
- Measurements can be made using smaller sample volumes
- Compact, portable system for real time measurement onboard a ship

Determination of LWCC pathlength:

Selecting the proper equipment is imperative when setting up your system. Here are a few considerations:

- Select the LWCC pathlength corresponding with the required absorption range. Here some reference values for different water types:
 - Fresh water with absorption range $> 4.0 \text{ m}^{-1}$
 - Coastal ocean waters with absorption range 1.0 m^{-1} — 4.0 m^{-1}
 - Open ocean with absorption range $< 1.0 \text{ m}^{-1}$
- Select the usable internal volume

Now, you can select components to complete your CDOM analysis system, depending on the selected LWCC.

The effective pathlength of WPI's LWCC is defined as the equivalent pathlength of the cell, if it is assumed that the LWCC follows strictly the Beer-Lambert law: $A = \epsilon \times c \times L$, where A is measured absorbance, ϵ the molar extinction coefficient, c is concentration and L the effective pathlength.

Typically, the longer LWCC pathlength is used to increase the sensitivity when the maximal absorbance values are supposed to be $< 0.1 \text{ AU}$ (Absorbance Unit). Inversely, when absorbance measurements are above 1.4 AU , the LWCC pathlength should be decreased to ensure that measurements still remain within the linear range of the LWCC detection system.

Absorbance measurements obtained with WPI's LWCC and Tidas S300 UV/VIS spectrophotometer are linear up to 1.4 AU . The measured absorbance can be converted to the spectral absorption coefficient $a(\lambda)$, commonly used in oceanography for CDOM measurements. Absorbance and spectral absorption are related by the formula: $a(\lambda) = 2.303 A(\lambda) / L$, where 2.303 is the conversion factor from decimal to natural logarithmic, $A(\lambda)$ is the absorbance at wavelength λ and L the LWCC pathlength.

LWCC pathlength selection table

LWCC Type	Pathlength (cm)	Noise (mAU)	Absorbance Range (mAU)	Absorption Range (m^{-1})	Internal Volume (mL)
LWCC-4010	10	< 0.1	0.5 - 1400	0.012 - 32.0	0.31
LWCC-4050	50	< 0.2	1.0 - 1400	0.005 - 6.4	1.57
LWCC-4100	100	< 0.5	2.5 - 1400	0.006 - 3.2	3.1
LWCC-3050	50	< 0.1	0.5 - 1400	0.002 - 6.4	0.125
LWCC-3100	100	< 0.2	1.0 - 1400	0.002 - 3.2	0.250
LWCC-3250	250	< 0.5	2.5 - 1400	0.002 - 1.2	0.625

Table 1. The useful absorption range calculation is based on the absorbance detection limits of the LWCC, considering a wavelength range of 300—700nm.

LWCC FOR CDOM MEASURING

The difference between the LWCC-3xxx and LWCC-4xxx series also relies on the difference in the internal volume of the flow cell and so the ease of handling.

LWCC-3xxx series

- Less ease of handling
- Use of Spartan Syringe filter for degassing and air bubble-free solutions
- Flushing with 3—5 times of internal volume to reach stable absorbance plateau
- Use of WPI's injection system (WPI **#89372**) to reach stable absorbance baseline
- Filtering through 0.2 µm filter (e.g. nylon) at low vacuum to ensure DCOM particulate

LWCC-4xxx series

- Easy to handle
- Higher volume gives more stable baseline of measured spectrum
- Sample and reference solutions can be inserted sequentially and separated by air bubbles
- Filtering through 0.2 µm filter (e.g. nylon) at low vacuum to ensure DCOM particulate

TIDAS S300 UV/VIS (190-720nm)

- Spectral resolution of 7 nm is ideally suited for measurements with all WP's LWCC flow cells
- Fitting data to a model from the entire measured spectrum allows calculation of discrete values
- Use of a photodiode array based detector with a very high signal to noise ratio
- Low baseline noise of 0.1 mAU peak to peak, improves absorbance measurements

For further methodological considerations, contact WPI or refer to the literature (e.g. Lefering et al. Applied Optics 56, 6357-6366, 2017).

System configuration

The CDOM-FRESH System > 4 m ⁻¹			
LOW VOLUME		HIGH VOLUME	
Product Description	Item #	Product Description	Item #
Liquid Waveguide Capillary Cell, 50 cm pathlength	LWCC-3050	Liquid Waveguide Capillary Cell, 10 cm pathlength	LWCC-4010
Photo Diode Array (PDA) Spectrophotometer System, UV/VIS (190-720nm) with integrated D2 H Lamps	505067	Photo Diode Array (PDA) Spectrophotometer System. UV/VIS (190-720nm) with integrated D2&H Lamps	505067
(2) UV-Enhanced Fiber Optic Cables, 1 m, 600 µm Core	FO-600-SMA1M	(2) UV-Enhanced Fiber Optic Cables, 1 m, 600 µm Core.	FO-600-SMA1M
Ministar Peristaltic Pump	MiniStar	PeriStar Pro Pump	PeriPro-4LS
LWCC Injection System	89372	Injector Kit	72100
TTL Control Module for Ministar and/or Peristar	503120	TTL Control Module for Ministar and/or Peristar	503120
UV-Enhanced Fiber Optic Cable	FO-200-SMA1M	UV-Enhanced Fiber Optic Cable	FO-200-SMA1M
(2) SMA Bulkhead feed through Connector/ Coupler	13395	(2) SMA Bulkhead feed through Connector/ Coupler	13395

LWCC FOR CDOM MEASURING

The CDOM-COAST System 1-4 m ⁻¹			
LOW VOLUME		HIGH VOLUME	
Product Description	Item #	Product Description	Item #
Liquid Waveguide Capillary Cell, 100 cm pathlength	LWCC-3100	Liquid Waveguide Capillary Cell, 50 cm pathlength	LWCC-4050
Photo Diode Array (PDA) Spectrophotometer System. UV/VIS (190-720nm) with integrated D2&H Lamps.	505067	Photo Diode Array (PDA) Spectrophotometer System. UV/VIS (190-720nm) with integrated D2&H Lamps	505067
(2) UV-Enhanced Fiber Optic Cables. 1 m, 600 µm Core.	FO-600-SMA1M	(2) UV-Enhanced Fiber Optic Cables. 1 m, 600 µm Core.	FO-600-SMA1M
Ministar Peristaltic Pump	MiniStar	PeriStar Pro Pump	PeriPro-4LS
LWCC Injection System	89372	Injector Kit	72100
TTL Control Module for Ministar and/or Peristar	503120	TTL Control Module for Ministar and/or Peristar	503120
UV-Enhanced Fiber Optic Cable	FO-200-SMA1M	UV-Enhanced Fiber Optic Cable	FO-200-SMA1M
(2) SMA Bulkhead feed through Connector/ Coupler	13395	(2) SMA Bulkhead feed through Connector/ Coupler	13395

The CDOM-Ocean System < 1 m ⁻¹			
LOW VOLUME		HIGH VOLUME	
Product Description	Item #	Product Description	Item #
Liquid Waveguide Capillary Cell, 250 cm pathlength	LWCC-3250	Liquid Waveguide Capillary Cell, 100 cm pathlength	LWCC-4100
Photo Diode Array (PDA) Spectrophotometer System. UV/VIS (190-720nm) with integrated D2&H Lamps.	505067	Photo Diode Array (PDA) Spectrophotometer System. UV/VIS (190-720nm) with integrated D2&H Lamps	505067
(2) UV-Enhanced Fiber Optic Cables. 1 m, 600 µm Core.	FO-600-SMA1M	(2) UV-Enhanced Fiber Optic Cables. 1 m, 600 µm Core.	FO-600-SMA1M
Ministar Peristaltic Pump	MiniStar	PeriStar Pro Pump	PeriPro-4LS
LWCC Injection System	89372	Injector Kit	72100
TTL Control Module for Ministar and/or Peristar	503120	TTL Control Module for Ministar and/or Peristar	503120
UV-Enhanced Fiber Optic Cable	FO-200-SMA1M	UV-Enhanced Fiber Optic Cable	FO-200-SMA1M
(2) SMA Bulkhead feed through Connector/ Coupler	13395	(2) SMA Bulkhead feed through Connector/ Coupler	13395

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- Kirkpatrick GJ, Orrico C, Moline MA, Oliver M, Schofield OM. Continuous hyperspectral absorption measurements of colored dissolved organic material in aquatic systems. *Applied Optics* 42, 6564-6568, 2003.
- Röttgers R, Koch BP. Spectroscopic detection of a ubiquitous dissolved pigment degradation product in subsurface waters of the global ocean. *Biogeosciences* 9, 2585-2596, 2012.



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