Determining CDOM Absorption Spectra in Diverse Coastal Environments Using a Multiple Pathlength, Liquid Core Waveguide System

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Abstract

We evaluated the accuracy, sensitivity and precision of a multiple pathlength, liquid core waveguide (MPLCW) system for measuring colored dissolved organic matter (CDOM) absorption in the UV-visible spectral range (370-700 nm). The MPLCW has four optical paths (2.0, 9.8, 49.3, and 204 cm) coupled to a single Teflon AF sample cell. Water samples were obtained from inland, coastal and ocean waters ranging in salinity from 0 to 36 PSU. Reference solutions for the MPLCW were made having a refractive index of the sample. CDOM absorption coefficients, a_{CDOM}, and the slope of the log-linearized absorption spectra, S, were compared with values obtained using a dual-beam spectrophotometer. Absorption of phenol red secondary standards measured by the MPLCW at 558 nm were highly correlated with spectrophotometer values (r > 0.99) and showed a linear response across all four pathlengths. Values of a_{CDOM} measured using the MPLCW were virtually identical to spectrophotometer values over a wide range of concentrations. The dynamic range of a_{CDOM} for MPLCW measurements was 0.002 – 231.5 m^{-1}. At low CDOM concentrations ($a_{370} < 0.1$ m^{-1}) spectrophotometric a_{CDOM} were slightly greater than MPLCW values and showed larger fluctuations at longer wavelengths due to limitations in instrument precision. In contrast, MPLCW spectra followed an exponential to 600 nm for all samples. The maximum deviation in replicate MPLCW spectra was less than 0.001 absorbance units. The portability, sampling, and optical characteristics of a MPLCW system provide significant enhancements for routine CDOM absorption measurements in a broad range of natural waters.

Keywords

Introduction

A major goal of ocean optics is to determine the contribution of water constituents to spectral absorption of light in the water column. Colored dissolved organic matter (CDOM), also known as yellow substance or Gelbstoff, is an important component in governing light propagation in coastal and open ocean waters (Bricaud et al. 1981; Morel 1988; Siegel and Michaels 1996). CDOM absorbs strongly in the UV and blue regions of the spectrum (Bricaud et al. 1981). Even at low CDOM concentrations, the chlorophyll *a* absorption peak of phytoplankton corresponds to significant CDOM absorption near 443 nm. Overlaps of pigment absorption spectra with CDOM absorption complicates the use of chlorophyll *a* retrieval algorithms that are based on remotely sensed ocean color (Carder et al. 1991; O'Reilly et al. 1998) and the development of phytoplankton production models (Arrigo and Brown 1996).

For river-dominated coastal margins, freshwater input is the principle source of CDOM and its distribution can often be described by conservative mixing with open ocean waters (Coble et al. 2000; Del Castillo 2000). However, Carder et al. (1989) showed that for several coastal areas, marine sources of CDOM coupled to primary production can significantly influence water optical properties. Other investigators (Miller 1994; Miller and Zepp 1995; Vodacek et al. 1997) indicated that production and distribution of CDOM could also be attributed to photochemical processes.

Although CDOM strongly influences ocean optical properties, remotely sensed spectra, and biogeochemical processes, the dynamics of CDOM in diverse aquatic environments remain largely undefined. This lack of understanding is due partially to a sparse global database of

CDOM absorption, especially at low CDOM concentrations. Moreover, the limited availability of such data is related to a lack of highly sensitive and portable optical systems that can provide measurements at sea, as well as current limitations in measurement methods and sampling protocols used commonly in CDOM absorbance spectroscopy (Hoge et al. 1993; Miller et. al. 2000).

Although spectrophotometers are used in the standard method for measuring CDOM absorption (Mueller and Austin 1995), the typical sensitivity of spectrophotometers with 10 cm optical cells (ca. 0.04 m^{-1}) is often low for CDOM absorbance measurements in many shelf and open ocean waters. Additional spectrophotometric methods have been proposed that include sample concentration (Carder et al. 1989) and longer pathlength cells (Peacock et al. 1994). Although these techniques extend the use of spectrophotometers to a wider range of water types, they potentially suffer from problems associated with sample handling (concentration and dilution), storage (Mueller and Austin 1995), and transport for laboratory analysis. These problems can prevent the routine collection and analysis of CDOM samples from remote waters.

One method used to increase the sensitivity of absorbance measurements is to increase the optical pathlength of the sample cell (e.g., from 1 to 10 cm). However, there are effective pathlength limitations in spectrophotometry due to scattering loss of light (Bricaud et al. 1981; Davies-Colley and Vant 1987). Alternatively, long pathlength liquid core waveguide technology can be used for high sensitivity absorbance measurements (e.g., Yao et al. 1998; Byrne and Kaltenbacher 1999; Zhang 2000). A liquid core waveguide (LCW) can provide optical pathlengths up to tens of meters and require low sample volumes (e.g. 100 µl - 10ml). A LCW is

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constructed to avoid light loss by constraining the light within the liquid core of the sample cell by total internal reflection at or near the cell wall. Light is reflected, or guided, when the refractive index of the liquid is higher than the refractive index of the cell wall or covering (cladding) (Belz et al. 1998; D'Sa et al. 1999; Byrne and Kaltenbacher 2000). There are two types of liquid core waveguides – Type I and Type II. Type I consists of a cell material of low refractive index; Type II consists of a low refractive index cladding separated from the liquid core by a transparent quartz tubing (Miller et al. 2000). Currently, there are no standard procedures established on how to select or apply small diameter (µm) Type I and Type II liquid core waveguides to absorbance spectroscopy (Byrne and Kaltenbacher 2001; D'Sa and Steward 2001).

D'Sa et al. (1999) describe the use of a 550 µm diameter, 0.5 m long LCW for measuring CDOM absorbance. Although they conclude that a LCW can determine CDOM absorption in different water types, they also present several problems and limitations of the existing technology. Here we demonstrate the use of a multiple pathlength, large diameter (2 mm) liquid core waveguide for determining CDOM absorption spectra in diverse aquatic environments representing a three-order magnitude range in CDOM concentration (a_{370} of $0.1 – 120$ m^{-1}). In addition, we address several problems reported by previous investigators (D'Sa et al. 1999; Miller et al. 2000; Zhang 2000), particularly waveguide stability and baseline offsets. The accuracy, sensitivity, and precision of CDOM absorption measurements made with the multiple pathlength, liquid core waveguide (MPLCW) are compared with results from a NIST (National Institute of Standards and Technology) traceable dual-beam spectrophotometer.

Methods

The MPLCW (Ultrapath, WPI Inc, Sarasota, FL, USA) consists of four optical paths (2.0, 9.8, 49.3, and 204 cm) selectable via a fiber optic switch. The four detection optical fibers are coupled to a single Teflon AF-2400 (DuPont Fluoroproducts, DE, USA) Type I cell with an internal diameter of 2 mm. The MPLCW was designed to provide accurate, highly sensitive UV-visible CDOM absorbance measurements over a broad range of CDOM concentrations in a compact portable system (Fig. 1). A transition to a larger diameter cell was made as preliminary experiments (Miller et al. 2000) demonstrated that a 2 mm Type I cell was not as susceptible to surface contamination and attached bubbles as with small diameter cells used in most LCWs (D'Sa et al. 1999). Consistent injection of 6.5 ml samples into the sample cell is achieved using a peristaltic pump. Incident light is provided by a color-balanced, tungsten light source (FO-6000, WPI Inc, Sarasota, FL, USA) developed for this application. The light source is a critical component of the integrated system that provides significantly higher UV (>370 nm) and blue light than standard tungsten sources. Incident light is coupled to the sample cell using a 600 µm fiber optic cable. Light exiting the waveguide is collected by a 400 µm optical fiber connected to a 16-bit photodiode array (PDA) fiber optic spectrometer (WAH6150, WPI Inc, Sarasota, FL). The spectrometer has a spectral range of 190 – 803 nm and a 3 nm (FWHM) spectral resolution. However, the effective spectral range for absorbance measurements was 370 – 725 nm due to the intensity spectrum of the light source.

Surface water samples were obtained from selected stations at eight locations representing inland, coastal, and oceanic waters (Table1). Samples were stored on ice in acid-washed amber

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plastic bottles until filtered. Samples were filtered using pre-rinsed 0.2 μm Nuclepore nylon filters and stored refrigerated (4 ^{o}C) in acid-washed amber glass bottles with teflon-lined caps. Filtration procedures followed the SeaWiFS protocols (Mueller and Austin 1995). Samples from La Parguera, Puerto Rico and the Mississippi River delta were prefiltered using GF/F filters then filtered through 0.2 μm filters. All samples were processed within 5 days of collection.

The accuracy of a Perkin Elmer Lambda-18 dual beam spectrophotometer was determined using NIST certified liquid absorption filters (SRM 931F). The standards, shipped in sealed ampoules, were analyzed following the procedures recommended by NIST. The results indicated that the spectrophotometer was accurate to the tolerances specified by NIST. The standards were not used to determine the accuracy of the MPLCW because the volumes were less than the required minimum MPLCW volume of 6.5 ml. To circumvent this limitation, a series of secondary standards were created using phenol red (phenolsulfonphtalein). All balances and volumetric equipment used in the dilution series were traceable to NIST. The secondary standards were measured in both instruments within two hours.

Absorption spectra using the Lambda-18 spectrophotometer were determined between 300 and 750 nm at 1 nm intervals. Milli-Q water was used in the reference cell. The samples and Milli-Q were maintained at the same temperature (25°C) using a water bath to avoid problems caused by differences in temperature. The water in the reference cell was replaced every five scans and the base line checked for instrument drift. Matched 10 cm cells were used for most samples except for the highest CDOM concentration when 1 cm cells were used to avoid sample dilution.

CDOM absorbance spectra measured using the MPLCW were determined between 370 and 725 nm at 3 nm interval normalized to a reference spectrum. Milli-Q water was used as a reference for freshwater samples. For seawater samples, salt solutions with the same refractive index as a sample was prepared using granular NaCl (Fisher Scientific) and Milli-Q water. The reference salt solutions were compared to Milli-Q absorbance values to insure that the solution was free of organic contamination. A reference spectrum, or baseline, was used when the average deviation of three additional reference absorbance spectra was less than 0.002 absorbance units (AU). A separate baseline was acquired for each sample. The integration time was set to maximize the signal measured at each optical path while avoiding over saturation of the 16-bit detector array. Integration times were 600 and 800 ms for the 1.99 and 9.84 cm paths, respectively, and 3800 ms for the 49.22 and 204 cm paths. The effective maximum absorbance for each pathlength was 2 AU. All spectra were corrected for dark current. Samples were brought to room temperature and placed in a clean glass bottle serving as a sample reservoir. The light source was turned on to stabilize at least 30 min prior to sampling. The effective pathlength for each optical cell was determined following the procedure of Belz et al. (1999). Pathlength was selected to optimize absorbance values in the 0 – 2 AU range at 370 nm. Because of the high sensitivity of the MPLCW, a clean sample cell devoid of cell wall contaminants and microbubbles is key to obtaining accurate baseline and absorption spectra. The MPLCW is cleaned by flushing the sample cell with a sequence of laboratory detergent (Cleaning solution concentrate, WPI Inc, Sarasota, FL, USA), high reagent grade MeOH, 2M HCL, and Milli-Q water. Trapped microbubbles are avoided by using a peristaltic pump to draw the sample into the sample cell.

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The spectral absorption coefficients, $a(\lambda)$ (m^{-1}) were obtained using the relationship

$$a(\lambda) = 2.303A(\lambda)/L,$$

where $A(\lambda)$ is the absorbance at wavelength λ and L is the pathlength in meters. Absorption data were corrected for baseline offsets by subtracting the absorption value at 700 nm. The spectral slopes, S (nm^{-1}), were determined using least-squares linear regression of log-linearized absorption data. The spectral range used to calculate S was 370 – 600 nm for all MPLCW data and most Lambda-18 spectrophotometer spectra except at low CDOM concentrations where absorbance values decreased to the detection limit of the spectrophotometer at about 425nm. For these samples, spectrophotometer S values were calculated from 300 – 420 nm.

Results and Discussion

Absorption coefficients measured using the Lambda-18 spectrophotometer and the MPLCW at a 558 nm absorption peak of the phenol red standards are shown in Fig. 2. The MPLCW absorption values were essentially identical to those measured using the spectrophotometer over a wide absorption range (0.05 – 118 m^{-1}). The largest difference, 5.96 m^{-1}, was observed for a_{558} greater than 80 m^{-1} compared to an average difference of 0.003 m^{-1} for phenol red concentrations less than 40 μM (equivalent to a_{558} of ca. 42 m^{-1}). The MPLCW absorption coefficients followed a linear response over the range of standard concentrations. Measurements were made using each of the four optical pathlengths as indicated by the different symbols in Fig. 2. The linearity of these measurements confirmed that the calculated effective pathlengths were correct and that the optical switch provided repeatable and stable alignment of the optical fibers in the waveguide.

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CDOM absorption at 400 nm and S for the field samples analyzed are given in Table 1. Water samples were obtained from inland, coastal and ocean waters ranging in salinity from 0 to 36 PSU. There is a close correspondence between the spectrophotometer and MPLCW derived absorption parameters. Absorption at 400 nm varied over three orders of magnitude corresponding to CDOM concentrations measured at an oligotrophic oceanic (PR3) and a fresh water hardwood marsh (NOE3) environment. Values of a_{400} measured with the MPLCW ranged from 0.03 to 81.63 m^{-1} and increased at stations influenced by rivers, whereas the Lambda-18 spectrophotometer values ranged from 0.06 to 84.8 m^{-1}. Values of the spectral slope S ranged from 0.013 to 0.02 nm^{-1} for the MPLCW and 0.012 to 0.18 for the Lambda-18 spectrophotometer. Trends in a_{400} and S observed for a particular environment (e.g., Lake Pontchartrain) were consistent between the two instruments.

CDOM absorption spectra and their log-linearized transforms are shown in Fig 3 for selected samples representing a range of CDOM concentration and salinity. These spectra are representative of the variability observed between the MPLCW and the spectrophotometer among all samples. Additional spectra are omitted for clarity, as they did not vary significantly from the trends exhibited in Fig. 3. In general, the MPLCW derived spectra showed a close 1:1 correspondence with the spectrophotometer data. This relationship was strongest for moderate-to-high CDOM concentration (Fig. 3A, C) where the spectral shape of the absorption curve showed only minor variation.

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Absorption spectra measured by the spectrophotometer were generally higher than MPLCW

values for the very low CDOM samples (Fig. 3B, D) with a maximum difference of 0.04 m^{-1} at

370 nm (sample PR3). Standard spectrophotometer measurements may over estimate absorption

due to scattering light loss from the sample media and particles smaller than 0.2 μm (Bricaud et

al. 1981; Aas 2001). CDOM absorption spectra obtained using the MPLCW showed minimal

spectral fluctuations (Fig. 4 A,B) and therefore do not require spectral smoothing as may be

necessary for spectrophotometric data. Complete internal reflection in liquid core waveguides

minimizes light loss due to scattering. The spectra obtained by the two instruments tend to

diverge at longer wavelengths. The most notable difference between the two instruments is the

lower signal-to-noise in the Lambda-18 spectrophotometer spectra resulting in a marked

decrease in the wavelength range at which the spectrophotometer data are above its detection

level (e.g., < 450 nm). The wavelength range over which an absorption coefficient or spectral

slope could be accurately derived from the spectrophotometer decreased with decreasing CDOM

concentration. The MPLCW measurements exhibited an exponential trend for absorption spectra

(Fig. 3B) or straight line for log-linearized spectra (Fig. 3D) to about 600 nm. To compensate for

this response, spectrophotometric measurements can be obtained at lower UV wavelengths than

used in this study and extrapolated to visible wavelengths assuming an exponential function

(Bricaud et al. 1981). In all cases, the spectral slopes calculated using MPLCW measurements

were valid from 370 – 600 nm and exhibited low spectral noise (Fig. 3D).

In addition to the similarity in the spectral curves, CDOM absorption coefficients measured

by the two instruments were highly correlated. The relationships at 370, 390, 400, 440 nm are

shown in Fig. 4. The correlation coefficient is significant ($p < 0.001$) for all four wavelengths (r

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> 0.99, n= 41). The largest variability was observed at 370 nm (Fig 4A, inset). The smallest deviation was at 440 nm (Fig 4D) with the exception of a_{440} at low CDOM concentration where the spectrophotometer measurements were again consistently higher than the MPLCW values. The relationship between CDOM absorption at 370 and 440 nm measured using two MPLCW pathlengths were statistically similar (p <0.001, paired t test, n =19) providing an independent assessment of the MPLCWs linear response.

Conclusions

This study demonstrated that a multiple pathlength, liquid core waveguide system could provide CDOM absorption spectra comparable, if not superior to those obtained with a NIST traceable dual-beam spectrophotometer. CDOM absorption values and the slope of log-linearized data measured by the two instruments were essentially identical over a wide range of CDOM concentration representative of samples from diverse aquatic environments. In oligotrophic waters or waters with low CDOM concentration, the long pathlength (204 cm) of the MPLCW provides significantly lower noise and greater sensitivity for absorbance measurements in the visible portion of the spectrum compared to a Lambda-18 spectrophotometer.

The MPLCW provided highly repeatable measurements in the 370 - 600 nm range thereby eliminating the need to extrapolate UV absorption to the visible region assuming an exponential fit. The use of a 2 mm diameter Teflon-AF cell drastically reduced cell contamination and the formation of microbubbles. Significant baseline offsets were reduced by using a Teflon-AF cell and a reference solution with a refractive index matching that of the natural sample. The magnitude of a baseline offset at 700 nm when observed was consistent with the offset measured

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in the Lambda-18 spectrophotometer spectra, with no deviations in spectral shapes. Consequently, there was a strong correspondence in absorption coefficients measured by the MPLCW and Lambda-18 spectrophotometer over a wide spectral range.

The MPLCW was interfaced to a low-cost PDA fiber optic spectrometer and a high intensity tungsten light source. The integrated system is compact and rugged for field use. The multiple pathlengths of the MPLCW are particularly useful for studies in river-dominated coastal environments where CDOM concentration frequently varies widely over a short geographic distance. Sample dilution or concentration is thus not required. The sampling protocols, particularly the method for sample injection, should be easily adaptable to a continuous flow-through system making detailed surface maps of CDOM absorption spectra possible.

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Figure Legends

Figure 1. Schematic diagram of the *Ultrapath* multiple pathlength, liquid core waveguide (MPLCW) showing system components and connections.

Figure 2. Absorption at 558 nm measured using the MPLCW and the Perkin Elmer Lambda-18 spectrophotometer at different concentrations of phenol red secondary standard. Inset shows the data for low values of a(558) at an expanded scale. The line is a linear fit to all data (y = -0.11 + 14.42x, r^2 = 0.99) Symbols identify the MPLCW pathlength used and the spectrophotometer samples.

Figure 3. Representative CDOM absorption spectra (A, B) measured by the MPLCW (dashed line) and the Perkin Elmer Lambda-18 spectrophotometer (solid line) and the corresponding log-linearized absorption spectra (C, D). The spectra plotted, from low to high values, in panels A and C are samples LP2, PRM2, LP7, PRM1, NOE2, and NOE6. In panels B and D, the spectra, from low to high values, are samples MRD39, MRD46, PR3, SF7, and PR5. Sample descriptions are given in Table 1.

Figure 4. Comparison of CDOM absorption coefficients at selected wavelengths in the UV (370, 390 nm: A,B) and visible (400, 440 nm: C,D) measured using the Perkin Elmer Lambda-18 spectrophotometer vs. the MPLCW for all samples. Insets show the relationship at an expanded scale for moderate absorption values. The line in each plot is the 1:1 correspondence.
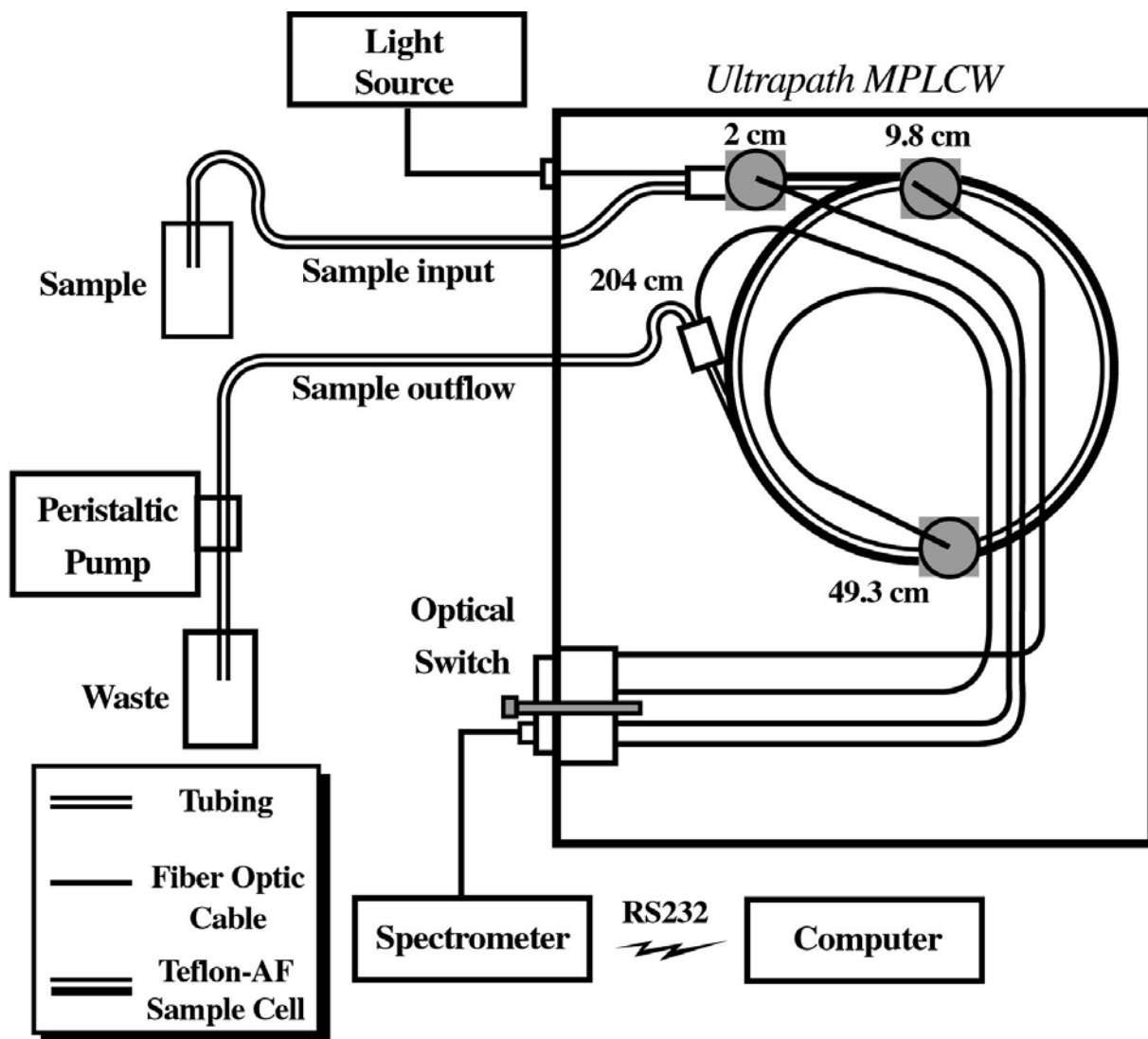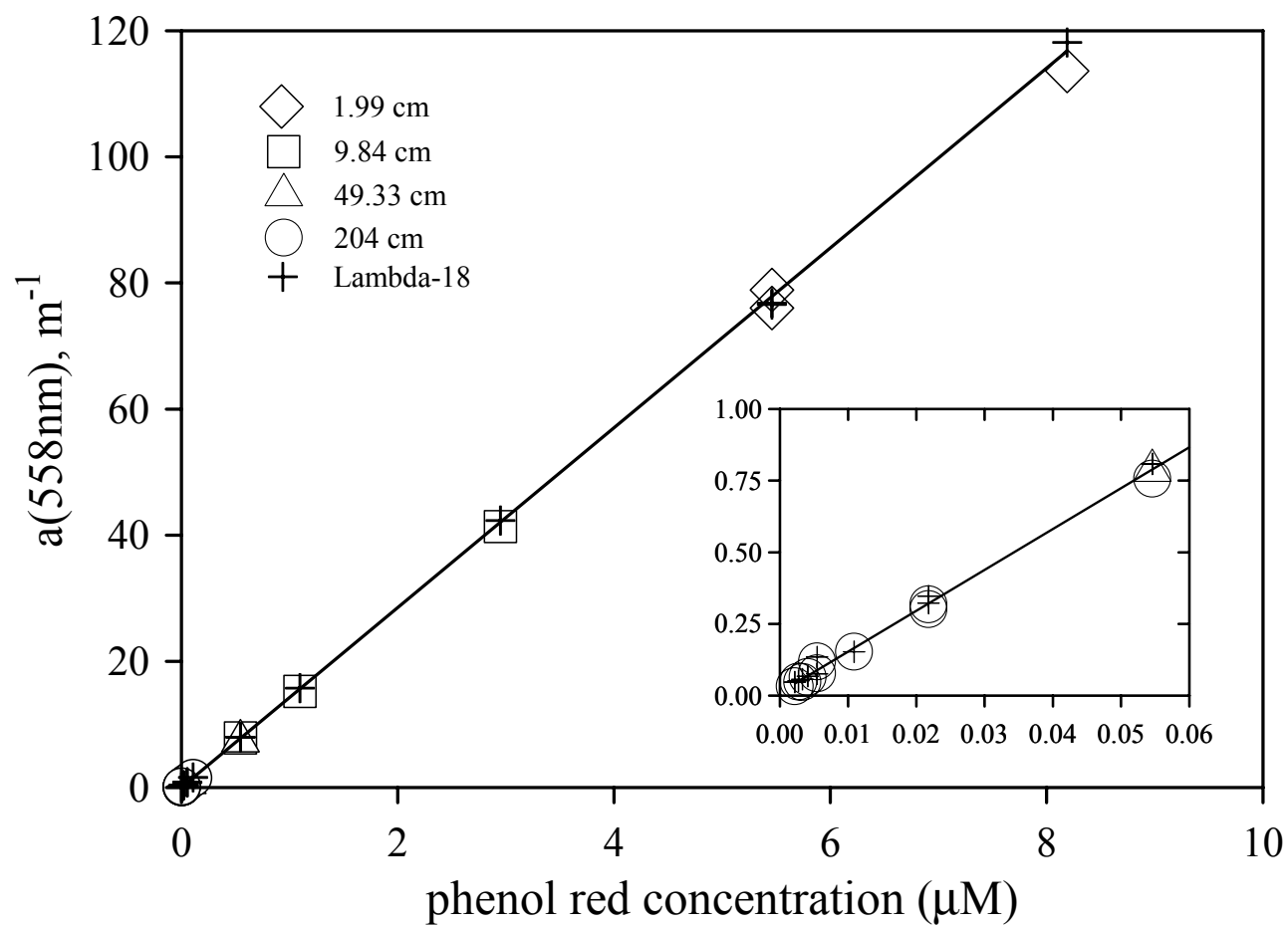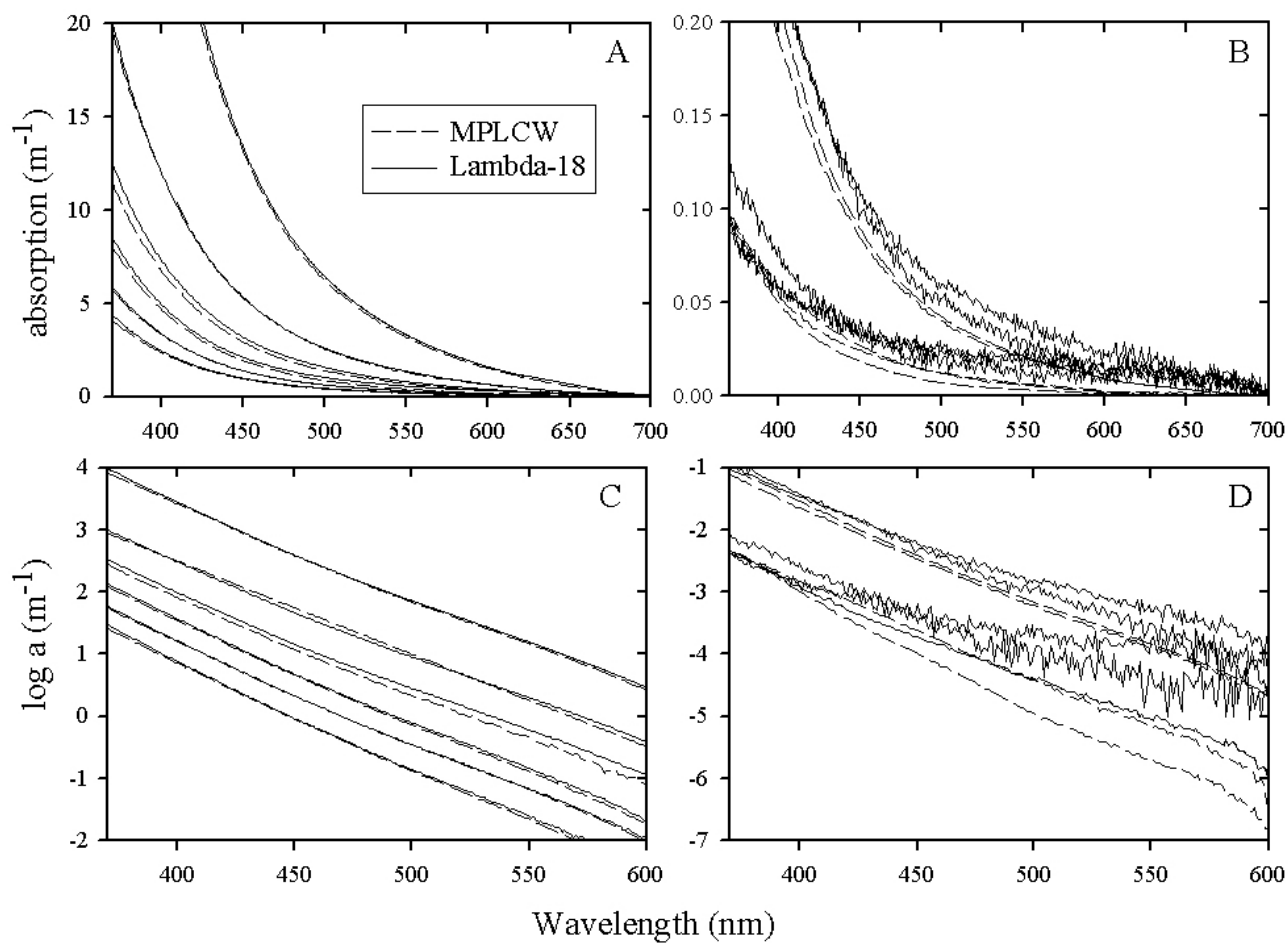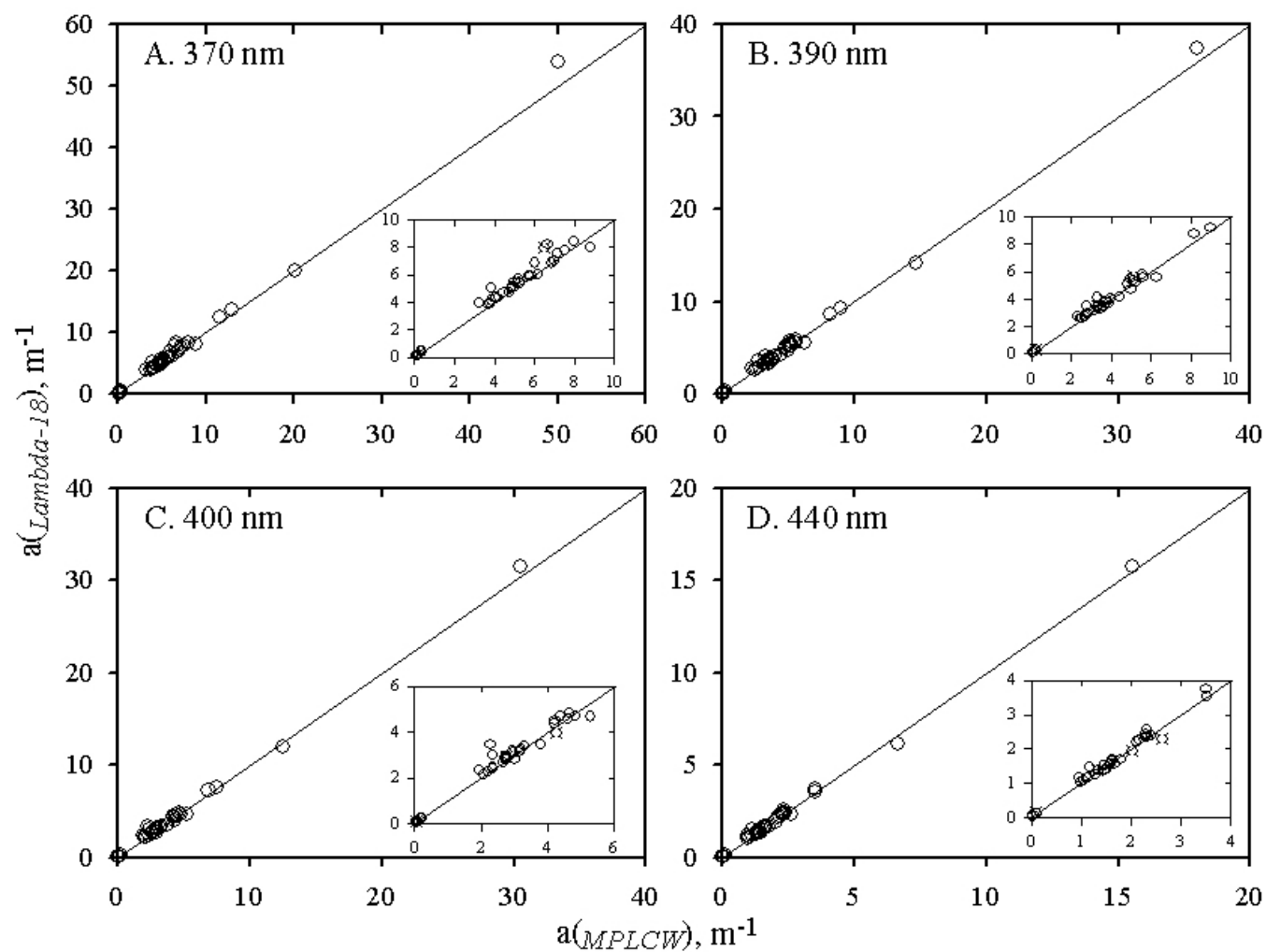
Fig. 1.

Fig. 2.

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Fig. 3.

Fig. 4.