# COMMENT

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# Use of liquid core waveguides for long pathlength absorbance spectroscopy: Principles and practice

For more than two decades liquid core waveguides (LCWs) have been used to enhance the sensitivity of spectroscopic absorbance measurements (e.g., Stone 1972; Waterbury et al. 1997; Yao et al. 1998; Yao and Byrne 1999). The principal desired characteristic of liquid core waveguides is confinement of light rays within the LCW liquid core when the refractive index (*n*) of the liquid core is higher than the refractive index of the surrounding tubing. However, not all light rays within an LCW are confined within the liquid core, and different types of waveguides can differ considerably in their waveguiding characteristics. The three most common forms of LCW in use today are glass capillary cells, flexible Teflon AF-2400 tubing, and quartz capillary cells coated with Teflon AF-2400. In a recent publication, D'Sa et al. (1999) observed offsets between absorption measurements using a quartz/Teflon LCW and those obtained with a conventional spectrometer. In this comment we describe the contrasting behaviors of (a) waveguides constructed solely of Teflon AF-2400 and (b) the waveguide of D'Sa et al. (1999) made of quartz with Teflon cladding. Through this descriptive analysis we are able to suggest a simple remedy for the problems noted by D'Sa et al. in LCW observations of colored dissolved organic matter (CDOM) in seawater.

The first type of waveguide considered in this work (Fig. 1) is a LCW composed solely of Teflon AF-2400 ($n_T \simeq 1.29$). A light ray (A) traveling through the waveguide can be expected to interact with the LCW's walls many times prior to arrival at the system's detector. Upon encountering the wall of the waveguide, the light ray (A) traveling within the liquid core can be either reflected (B), or transmitted (C) within the LCW wall. Transmitted rays subsequently encountering the outer wall of the LCW can be either reflected (D) or transmitted (E). Reflected ray D, upon encountering the Teflon/water interface, can again be transmitted (F) and returned to the waveguide's liquid core.

A critically important aspect of the behavior of a Teflon AF-2400 LCW ($n_T \simeq 1.29$) with a water core ($n_W \simeq 1.335$) is the existence of complete internal reflection (no light propagation within the solid LCW wall) when $\theta_1 \geq 76°$. Confinement of light entirely within the waveguide's liquid core has two important consequences:

1. The effective optical pathlength is essentially independent of wavelength. Pathlength differences occur only as a result of small differences in the launch angles of light at various wavelengths. For reflected light of any wavelength, the light path is independent of the $n_T/n_W$ ratio. In contrast, for transmitted light, $\theta_2$ is dependent on $n_T/n_W$ through Snell's Law (i.e., $n_W \sin \theta_1 = n_T \sin \theta_2$), and the cumulative length of travel within both the solid LCW wall and the liquid core is wavelength dependent.

2. Absorbance observations are unaffected by small changes in the liquid's refractive index (caused, for example, by variations in the salinity of seawater samples). As long as all light propagation is confined within the LCW's liquid core, variations in light transmission associated with refractive phenomena at optical interfaces are unimportant.

Although some light will propagate into the Teflon wall, propagation of this light to the detector can be prevented by submerging the Teflon cell in water or coating the cell with a medium of higher refractive index (e.g., heat shrink tubing). In either case, since $n_T < n$ (cladding) light radiating through the Teflon wall will effectively exit at the outer surface. No internal reflection can occur at the outer wall for light propagating into a more optically dense medium. This is an ideal situation because virtually all radiation reaching the detector will have traveled solely within the liquid core.

A second type of waveguide, used by D'Sa et al. (1999) to observe the absorbance properties of CDOM in seawater, is shown in Fig. 2. In this case, the LCW liquid core is surrounded by quartz ($n_Q \simeq 1.46$), which is itself surrounded by an amorphous polymer cladding (Teflon polymer, $n_P \simeq 1.31$). Since $n_Q > n_W$, complete internal reflection does not occur at the waveguide's water/quartz interface for any incident angle, $\theta_1$. Therefore, essentially all of the light initially introduced to the LCW liquid core travels both in the liquid core and in the quartz itself. Light is very effectively trapped within the quartz walls of the LCW because $n_Q$ is much larger than both $n_W$ and $n_P$. Light that does exit the quartz wall of the waveguide will propagate within the liquid core and again within the quartz LCW wall, in a process that will involve a large number of traverses of the water/quartz interface. There are two simple and very important consequences of this LCW design:

1. Since the refractive index of any substance is wavelength dependent, the angle ($\theta_2$) of the light ray entering the quartz wall of the LCW varies with wavelength. On this account, light paths within this LCW are wavelength dependent and the effective aqueous pathlength of the LCW will be wavelength dependent. This effect was noted in a comprehensive study by Tsunoda et al. (1989). Tsunoda et al. observed that effective aqueous path lengths at 632.8 and 780 nm differed by 25 cm in a 90-cm glass capillary cell, and that effective cell lengths were both longer ($\lambda$ = 632.8 nm) and shorter ($\lambda$ = 780 nm) than the physical length of the cell. Simple application of Beer's law to this system will

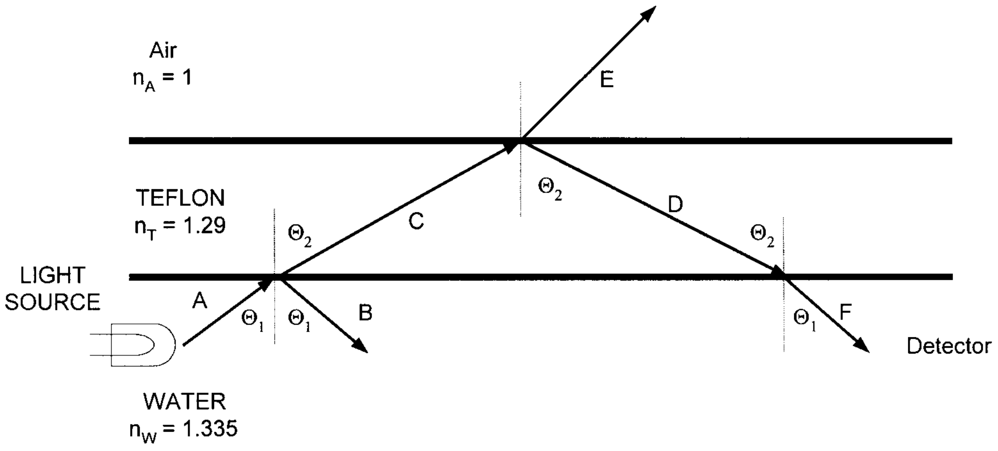

Fig. 1. Light transmission in a pure Teflon AF-2400 waveguide: light ray (A) within the liquid core is shown being (B) reflected and (C) refracted at the liquid core/Teflon interface. Light path B is strongly dominant in this type of waveguide due to complete internal reflection when $\theta_1 >$ 76°. The refracted ray (C) is strongly reflected at the Teflon–air interface and returned to the liquid core along the path D and F. Although only a small fraction of light energy escapes the system (ray E) when the Teflon AF-2400 is in air, when the Teflon AF-2400 is surrounded by water, light transmission along path E is strongly favored and very little light follows paths D and F. In this case only reflected rays (B) transmit light through the system.

not be accurate since ''a nonlinear calibration curve would be expected'' (Tsunoda et al. 1989).

2. Since the light paths taken by all light rays within the LCW are dependent on the ratio $n_Q/n_W$, and $n_W$ is dependent on salinity, light paths within the LCW are salinity dependent. Unless the salinities of reference samples and natural samples are carefully matched, measured absorbances can exhibit both positive and negative deviations from reference samples. Baseline offsets noted by Green and Blough (1994) between freshwater references and seawater absorption measurements were attributed to such refractive index differences. Green and Blough concluded that ''. . . refraction of the uncollimated lamp can result in significant focusing or defocusing of the light beam through the cell, causing more or fewer photons to reach the detector.'' This focusing effect is wavelength dependent and inevitable in a quartz/polymer cell since light is not confined solely within the liquid core.

The simplicity of pure Teflon waveguides compared to

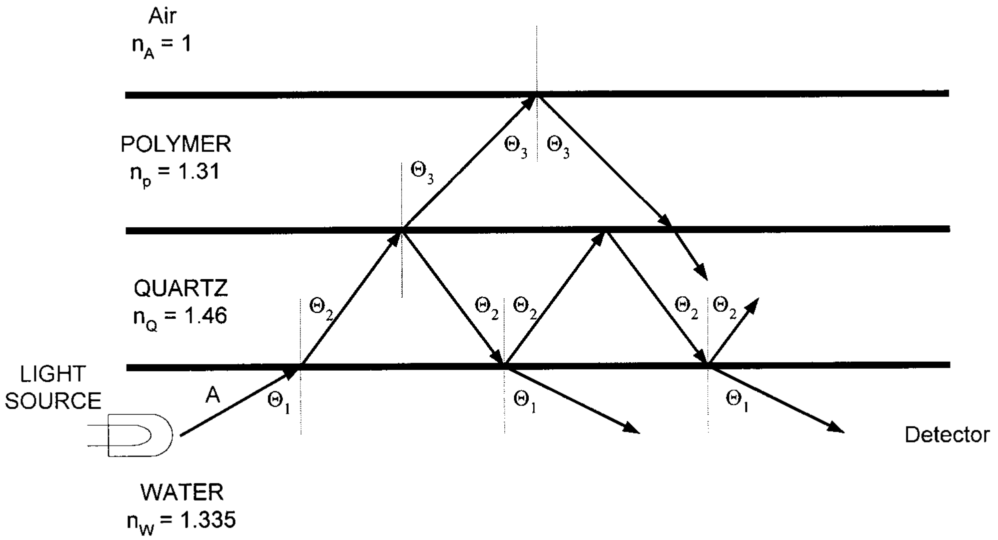

Fig. 2. Light transmission in a quartz-polymer waveguide: light ray A is shown being refracted into the quartz wall of the waveguide. Very little light is reflected since $n_W < n_Q$. Light is effectively trapped within the quartz region because $n_W < n_Q > n_P$. The small fraction of light transmitted to the polymer is efficiently reflected at the polymer/air interface and returned to the quartz. Light that escapes the quartz wall via the liquid core travels through the liquid only a short distance until it again intersects the quartz wall. Light propagation solely within the liquid core does not occur in this type of waveguide since no complete internal reflection can occur when $n_W < n_Q$.

quartz/polymer waveguides offers strong advantages in the measurement of CDOM in seawater. The need to carefully match the refractive indices of natural and reference solutions (very challenging in estuarine waters) can be mitigated or eliminated entirely. It is highly desirable to conduct CDOM measurements using waveguides that do not propagate light across optical interfaces. The best means of achieving this objective is the use of waveguides in which the liquid core is in direct physical contact with walls that have a lower index of refraction than water. Additionally, we note that if such an LCW (i.e., $n_T < n_W$) is itself immersed in water, any light propagating within the Teflon wall will efficiently exit the LCW. In this case, even for poorly collimated light, only light traveling solely within the LCW liquid core will reach the detector. We are currently using an LCW of this design for in situ measurements of analytes in seawater (Steimle et al. pers. comm.). As a final note on the practicality of these waveguides. A 50-cm quartz/polymer LCW is currently sold commercially for roughly US $1300, whereas a 50-cm length of a Teflon AF-2400 LCW costs approximately US $100.

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# Liquid capillary waveguide application in absorbance spectroscopy (Reply to the comment by Byrne and Kaltenbacher)

Liquid capillary waveguides (Fig. 1b) have been used in marine applications to determine dissolved characteristics of seawater (D'Sa et al. 1999; Zhang 2000). Byrne and Kaltenbacher (2001) in comparing optical characteristics of type I (Fig. 1a) and type II (Fig. 1b) waveguides attribute spectral nonlinearities in absorbance measurements with type II waveguides to the quartz capillary tubing. We show in this study through a theoretical analysis that in the absence of imperfections in the quartz capillary or the presence of scattering particles in the solution being measured, light cannot be trapped in the waveguide quartz wall as suggested by Byrne and Kaltenbacher. In addition, we present results from laboratory observations that clearly indicate linearity over a wide absorbance and spectral range, including absence of wavelength dependence in the absorption measurements with the quartz/Teflon waveguide. A direct comparison of the two waveguide systems discussed by Byrne and Kaltenbacher was not possible, as no experimental results were shown by them to support their hypothesis.

In D'Sa et al. (1999), we use a quartz capillary tubing ($n_Q$ = 1.46 at 589 nm) with an inner diameter of 550 $\mu$m, a wall thickness of 50 $\mu$m having an outer Teflon AF coating ($n_p$ = 1.31 at 589 nm) and an effective path length of 45.9 cm. Fused silica optical fibers having core diameter of 400 $\mu$m and a numerical aperture (NA) of 0.22 (589 nm) are used to couple light into and out of the type II waveguide in such a way that no light is coupled into the front face of the high refractive index fused silica quartz capillary wall (Fig. 1b). For seawater, the half-angle $\alpha$ of the source optical fiber emission cone (D'Sa and Lohrenz 1999) is related to its NA in air ($\sin \alpha'$) by the relation

$$n_{sw}\sin(\alpha_{sw}) = \sin(\alpha'). \quad (1)$$

For the real index of refraction of seawater ($n_{sw}$ = 1.339), we obtain $\alpha_{sw}$ = 9.45°, and thus $\theta_1$ = 80.55° (for the sum of all light rays coming from the fiber, $\theta_1$ can vary from 80.55° to 90° for a parallel light ray [refer to Byrne and Kaltenbacher, fig. 2]). At the boundary between seawater and the quartz wall, the relation between $\theta_1$ and $\theta_2$ is given by

$$\sin \theta_2/\sin \theta_1 = n_{sw}/n_Q. \quad (2)$$

Substituting values in Eq. 2, we obtain $\theta_2$ = 64.7° for $\theta_1$ = 80.55° and $\theta_2$ = 66.5° for light emitted along waveguide axis with $\theta_1$ = 90°. Thus, it can be assumed that for an optical