



Application of Newton's Zero Order Caustic for Analysis and Measurement: Part-I Absorbance

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Authors' contributions

This work was carried out in collaboration among all authors. Authors AAG and LN designed the study and wrote the first draft of the manuscript. Authors CJ, HH, VO and AAG measured and analyzed the results. Authors LN and VM reviewed the optical ray tracing and managed the literature searches. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

When light is incident upon a liquid solution droplet containing a light absorbing solute and it is formed into a spheroid shape, absorbance can be measured and related to concentration of the light absorbing species in a manner analogous to standard spectrophotometry. However, the spheroid sample acts as a focusing lens through the method of Newton's zero order caustic resulting in a higher intensity of light within the sample and light that reaches the detector. As a result, linearity of the Beer-Lambert law can be observed without stray light correction at values of absorbance greater than 1. Also, fluorescence can be observed using lower excitation energy than what would normally be required. In order to illustrate measurement and detection, using Newton's zero order caustic, solutions of two food dyes (Brilliant Blue FCF and tartrazine) were studied using matching red (660 nm) and blue (430 nm) photodiodes.

Keywords: *Newton's zero order caustic; absorbance; tartrazine; ray tracing.*

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ABBREVIATIONS

x_s = distance between the point source and the center of the water drop being illuminated; a = minor (orthogonal to light source) radius of a spheroid liquid sample; b = major axis of a spheroid liquid sample; A = absorbance; $\log(I/I_0)$; Yellow Dye #5 = tartarazine; Brilliant Blue FCF = Blue #1; PTFE = polytetrafluoroethylene; PBT = Polybutylene terephthalate; Cartesian coordinates = (x,y,z) ; Radius of spheroid = R ; light intensity = I ; OpAmp = operational amplifier.

1. INTRODUCTION

Analysis of samples using optical methods generally rely on the use of a light source with well-characterized properties that are uniform spatially, to the extent technologically possible. On the other hand, the natural world lets us experience light in complex forms and frequently gives rise to unique phenomena when sunlight is transmitted through water, such as a rainbow. Rainbows are one form of an optical caustic, which is the modern phrase that describes when light rays are reflected or refracted by a curved surface. Leonardo Da Vinci is considered to have been the first to sketch the light rays due to an optical caustic ca. 1508. In Opticks (1704-1730), Sir Isaac Newton discussed the effects of refraction with or without reflection through water droplets and described how these phenomena produce rainbows. Modern day computer graphics techniques rely on ray tracing algorithms that can produce optical caustics in order to depict realistic scenes showing light refraction and reflection such as in the shimmering of water waves in the bright sunlight and the pattern produced by a bright light shining at an angle from above a glass of water, a wine glass or at the bottom of a cup. Applications of optical caustics in lighting include early Islamic and Byzantine (ca. 8-10th century) light fixtures that used water inside a glass bowl, along with a layer of oil and a wick for the flame [1] in order to project light in a specific direction. A sealed water filled bulb and gas lamp were used ca. 1700s to produce a beam of light for lace making. In the modern era, optical caustics have been employed for inspecting materials for stresses and defects [2,3]. More recently, an ordinary optical microscope has been demonstrated to image individual nanoparticles [4] by closing down the aperture of the halogen lamp source. However, the use of optical caustics for the analysis of a liquid solution is not described in the literature, and this is the subject of our paper.

Several researchers have noted the unique properties when light is refracted through a spherically-shaped liquid sample. Johannes Kofler's thesis [5], while intended for understanding the field distribution of light focused by microspheres, showed how the Bessoid integral derived diffraction catastrophe theory can be used to model light intensity due to caustic refraction (see Equation 1).

$$I(R, Z) = \frac{1}{2\rho} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i(Rx_1 + Z\frac{x_1^2 + y_1^2}{2} + \frac{(x_1^2 + y_1^2)^2}{4})} dx_1 dy_2 \quad (1)$$

Kofler's 3-D mathematics and ray trace simulations point to the production of a high intensity field along the axis of the spherical particle, reaching 900 times the incident light intensity. This work is particularly instructive because ray tracing alone cannot provide accurate intensity distributions since the caustic yields zones of unrealistic, infinite intensity zones for this approach. The work of Horvath [6] on sunlight refraction of water drops on leaves also

shows that a uniform source produces zones of very high intensity for spheroid or hemispherical water drops. Lock and McCollum [7] debated the existence of the so-called "Newton's zero-order rainbow", providing ray trace analyses and experiments that showed how zero-order rainbows can be produced without reflection in a spherical water drop. Interestingly, they also noted that a point source placed at the paraxial focal point of a spherical drop would result in a system akin to a searchlight.

In the first of this 3-part series, the detection of solutes in water by absorbance using light formed into an optical caustic within the sample itself is discussed and experimental results are compared with measurements from a standard UV/VIS spectrophotometer. Motivating this work is the potential to lower equipment cost and power consumption due to the intensification of the beam being detected and the built-in lensing effect due to the use of curved sample surfaces. Moreover, introducing curved surfaces in an optical system also allows for fluorescent and light scattering measurements, which are discussed in the second and third parts of this series.

2. MATERIALS AND METHODS

2.1 Sample Stage

The sample stage consisted of a PTFE coated slide with 30 wells of 3 mm diameter (Tekdon Inc., Myakka City, FL), which pinned drops of 120 microliters of the aqueous solution sample forming a spheroid shape and produced the studies with Newton's zero order caustic, without the need of a sample container. Each multi-well slide can measure 5 different samples and each position can be used for multiple tests of the same sample solution. At room temperature, the optical signal changes very slowly due to evaporation since the aqueous drop is pinned into a spheroid shape rather than a thin film of high surface area. The spheroid shape of the samples was characterized using Image J (<http://rsbweb.nih.gov/ij/>) and found by edge analysis and measurement to have the ratio of 1.5 for water as well as all solution concentrations, due to the balance between pinning and surface tension effects. This leads to accurate and reproducible readings from an open-air sample, even though solute concentration alters the liquid surface tension. For this initial study of optical caustic readings, an open-air sample avoids the need to correct for refraction of light from a curved sample container.

2.2 Photodiode Device

Light emission and photodetection were accomplished using two sets of matched photodiodes with internal micro-lens and PBT housing (Industrial Fiber Optics, Tempe, Arizona): Red, 660 nm peak wavelength and Blue, 430 nm peak. The photoemitter was powered by a standard, constant voltage, DC circuit based on the manufacturer's recommended value of 4.5 Volts at 35 mA. The photodetector was connected to an OpAmp (LF351, Fairchild Semiconductor, San Jose, CA) in open circuit mode using reverse bias. Volt or panel meters were used to measure the voltage at the photodetector. Voltage measured for a particular sample was divided by the voltage for pure water in order to calculate the relative absorbance. Due to the open geometry of measurement in this system, alignment of the caustic prior to taking a reading was performed in one of three different ways, each giving consistent results. First, alignment was accomplished by visual inspection of the caustic on the barrel of the detector. Secondly, alignment was done visually using a small curved mirror on the opposite side of the detector in order to magnify the view of the

caustic. Finally, a small optical fiber placed inside the housing and directly above the detector was used with an external LED to signal alignment to the operator. A photodarlington was used in conjunction with the optical fiber in order to detect the weak signal from the fiber when the sample is aligned.

2.3 Spectrophotometry

Results using the optical caustic detection system were compared to absorbance measurements taken by a spectrophotometer (model USB2000 Miniature Fiber Optic Spectrometer, Ocean Optics). This spectrophotometer accepts incident radiation transmitted through a single-strand optical fiber (400 μm fiber diameter, UV/VIS Laboratory-grade Patch Cord Optical Fiber Assembly, Ocean Optics) and disperses it via a fixed grating across a 2048-element linear CCD array detector. The operating software (Spectra Suite, v. 2.0.109, Ocean Optics) runs on a Mac Pro laptop (Apple, Cupertino, CA). An achromatic collimating lens (350-2000 nm) (model 74-ACR, Ocean Optics) was used to collect the incident light, which is then transmitted through the optical fiber to the grating. Plastic or Quartz cuvettes were used with an optical path length 1 cm. Spectra were taken based on an average of 50 scans at 20 milliseconds per scan.

2.4 Chemicals and Reagents

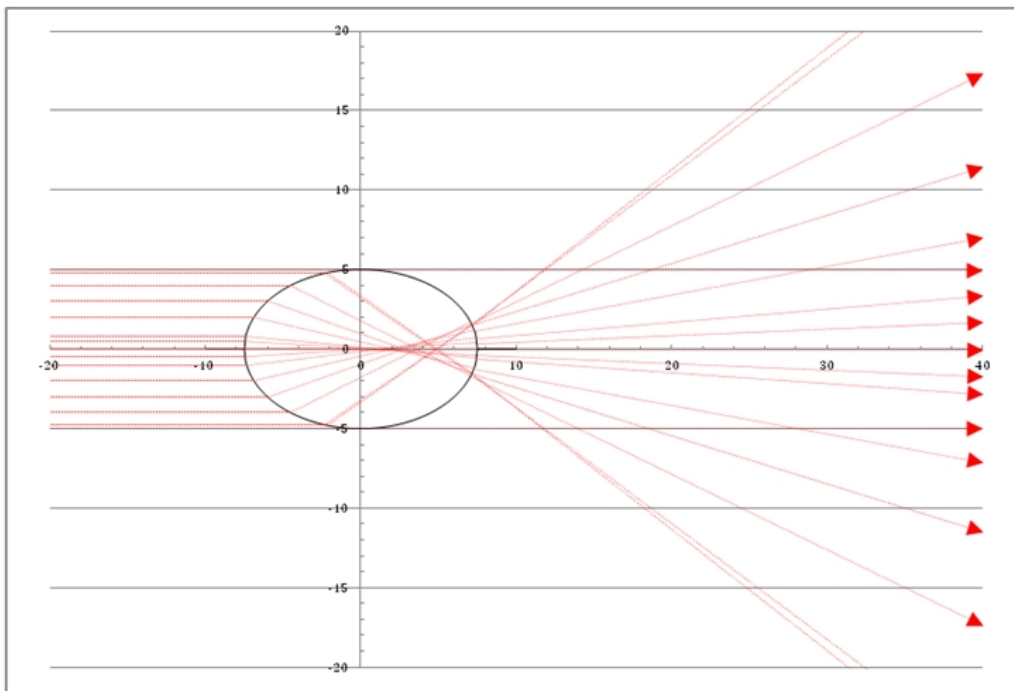
Two solutes were investigated: FD & C Blue #1 (Brilliant Blue FCF) and tartrazine (Yellow Dye #5). Blue #1 is a colorant for foods, has a color index of 42090, is soluble in water, and exhibits a maximum absorbance at 628 nm. Tartrazine is also a colorant for foods, has a color index of 19140, is soluble in water, and exhibits a maximum absorbance at 427 nm. Tartrazine fluoresces when excited by a relatively broad band of UV light (280-380 nm), generating a strong fluorescent light at 565 nm [8].

3. RESULTS AND DISCUSSION

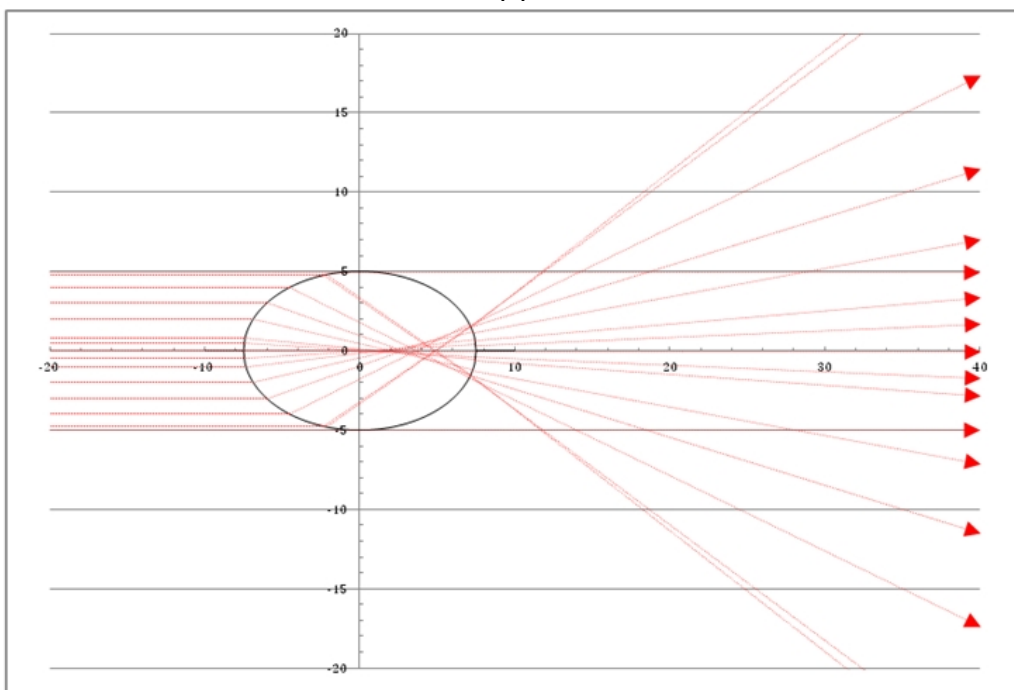
3.1 2-D Ray Tracing

The optical caustic housing was designed to be a unibody construction, which resulted in the integration of a 30-well microscope slide with an acrylic holder for the photodiodes. The distance between the source and the center of the drop is crucial in understanding the way light refracts into the detector window. Lock [7,9] derived equations for the ray tracing of light with no reflections through a sphere illuminated from a point source and a uniform field, as well as a spheroid illuminated by a uniform field. His equations were used to generate the 2-D ray traces in Fig. 1, and the Figs. 1a-1c are consistent with the ray traces given in his work. While Lock provides 2-D results for an ellipse, he does not show ray tracing for this geometry illuminated by a point source. Also, it should be noted that using an ellipse is an approximation of the spheroid geometry, and it is used only as a qualitative guide. Fig. 1a illustrates the experimental system used where a point source was placed at a distance from the center of a spheroid water drop ($b/a = 1.5$) of four times the drop minor axis ($x_s/a = 4$), and a uniform light source is shown for comparison in Fig. 1b. In Fig. 1c, a spherical drop illuminated with a point source is shown, also for comparison purposes. The photodetector window is placed at $x_s/a = 8$ in the experimental system because while the photodetector housing has a 3 mm diameter opening at $x_s/a = 4$, the collecting lens is located at $x_s/a = 8$. Ray tracing illustrates a major difference between a spheroid and a spherical sample, namely that the optical caustic is formed within rather than outside the liquid. This

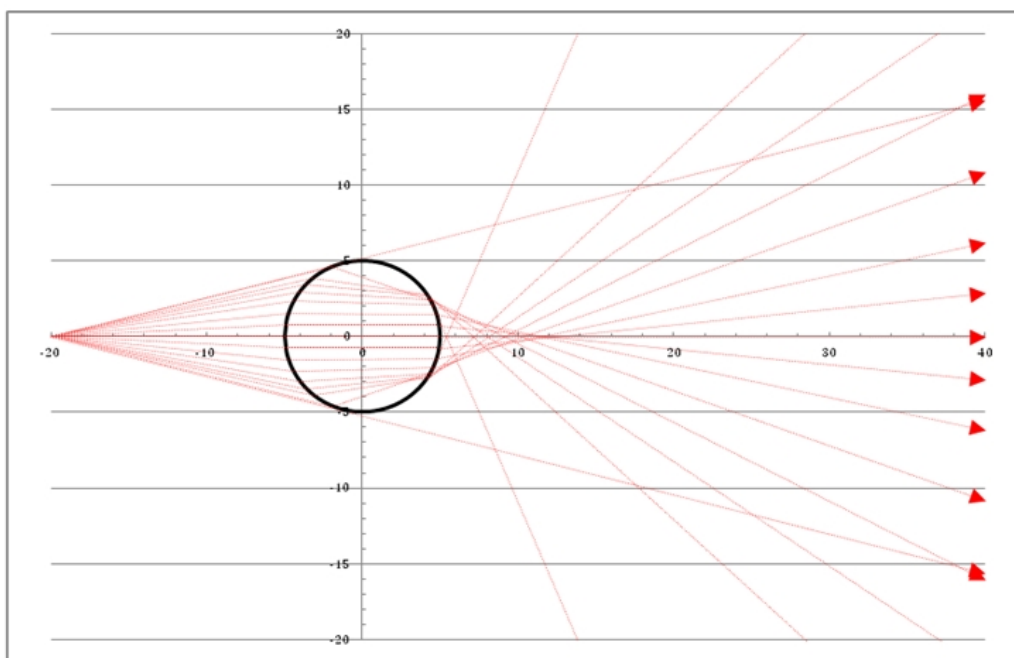
significantly influences the capabilities of the system since the forward intensity is very high [9], allowing a low power light to be used for measuring liquid samples with high absorbance.



(a)



(b)



(c)

Fig. 1. 2-D ray tracing comparison for a point source (a) and a uniform source (b) being refracted and the resultant rays exiting the spheroid, while (c) is for a point source for a sphere. An ellipse is assumed to represent a spheroid, however the 3-D geometry is more complex due to a lack of symmetry. All shapes form Newton's zero order caustic, but for the spheroid it is within the liquid sample. The spheroid has a b/a ratio of 1.5. Fig. 1b represents the optics of the experimental platform used to collect data

Calibration of the optical caustic system, with repeat measurements of water droplets, was carefully studied to verify the capabilities of the three caustic alignment methods described in the experimental section. All alignment systems yielded signals for a spheroid drop of deionized, 0.2 micron filtered water with $\leq 2\%$ variation (based on random testing of 50 slides from 10 different boxes, 5 samples per slide). This variation remained fairly consistent with operator and over multiple photodiodes, electronics, and acrylic slide holder. For a 120 microliter drop of deionized, 0.2 micron filtered spheroid drop of water the average value was 7.2 volts for the Red photodiode and 2.0 for the Blue photodiode, with a minimum reading of 0.0 when the emitter is blocked, for each photodiode pair. It should be noted that the difference in refractive index of water between these two wavelengths is very small ($< 0.8\%$) and only very slightly alters the 2-D ray trace diagram shown in Fig. 1a.

3.2 Brilliant Blue FCF

Fig. 2 shows the optical caustic measurement of absorbance for the food coloring Blue Dye #1 (Brilliant Blue FCF) as a function of concentration. The Red photodiode and matched detector used to measure Blue Dye #1 produced a wide linear concentration vs. Absorbance range that generally follows the Beer-Lambert law. As described in the experimental section, a water droplet is used as a reference, and each data point represents triplicate measurements of the voltage reading from the amplified photodiode detector.

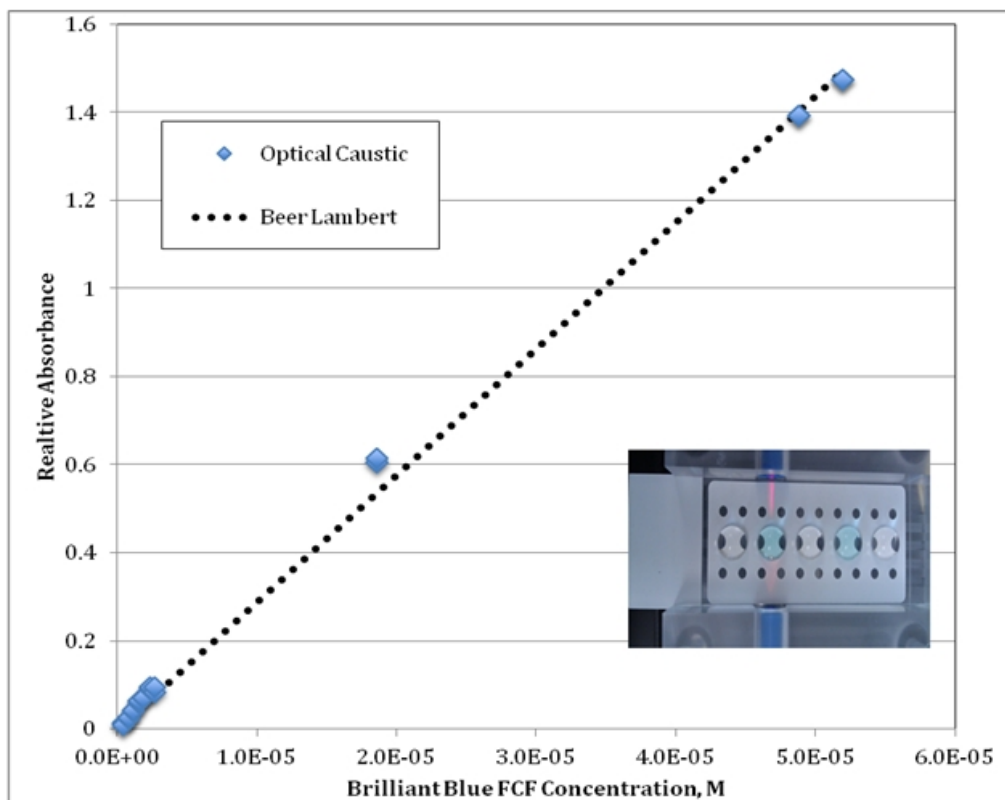


Fig. 2. Measurement of absorbance using a sample chamber that shapes a solution of Brilliant Blue to form an optical caustic when illuminated by light from a red LED (maximum at 630 nm). Absorbance follows a nearly linear Beer-Lambert law dependence with dye concentration even at relatively high concentration. The insert shows 5 samples: 3 water drops and 2 Brilliant Blue FCF aqueous solutions. The light from the lower photodiode is intensified within the drop and exits in a higher intensity beam to the upper photodiode, which is the detector

In Fig. 3, for the spectrophotometer, the Beer-Lambert law is followed at concentrations below 20 micromoles per liter, but the data deviate significantly from linearity at concentrations above 40 micromoles per liter. This deviation from the Beer-Lambert law is generally known to occur when absorbance exceeds a value of 1, unless corrections are made due to stray light. The manufacturer of the instrument does provide a correction factor algorithm and other suppliers provide calibration standards, but for the purposes of this study they were not employed in order to more directly compare the two optical platforms.

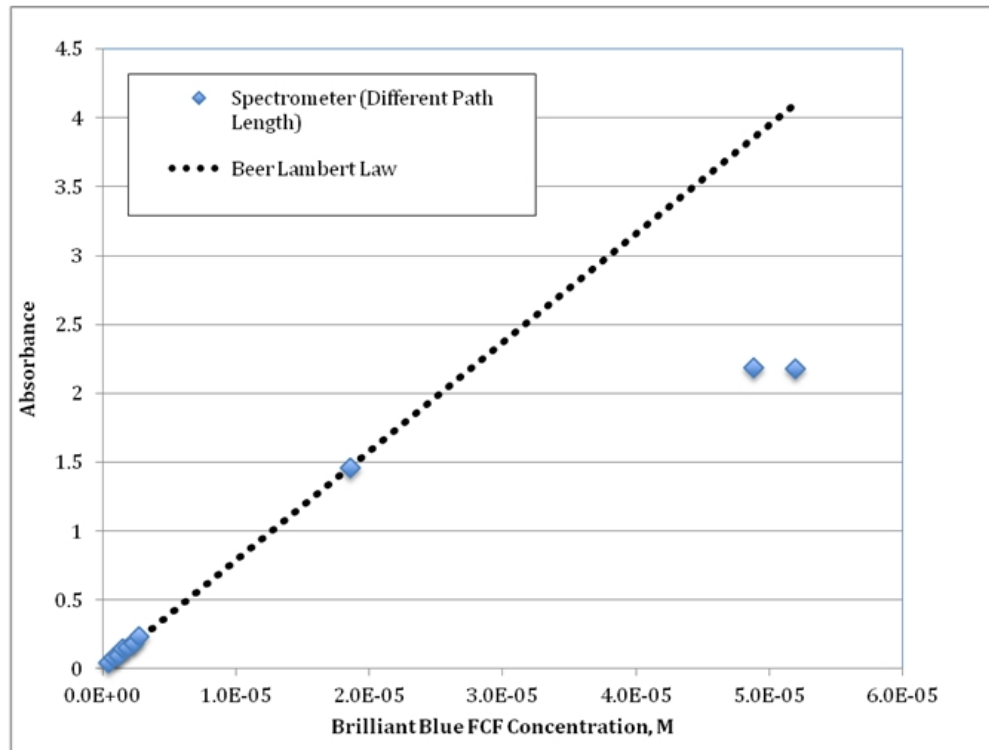


Fig. 3. Brilliant blue absorbance versus concentration measured at the absorbance maximum using a spectrophotometer and a rectangular cuvette. Deviation from Beer-Lambert law is seen at absorbance above 1.5

Upon further inspection of the results in Figs. 2 and 3, it is evident that the spectrophotometer follows the Beer-Lambert law more accurately at lower concentrations than the optical caustic device, but at higher concentration the optical caustic data deviate only slightly from the Beer-Lambert law. These differences stem in part from several features of the optical caustic system, namely that there is a high intensity increase in the middle zone of the droplet, there are variations in intensity over the cross section of the sample, and that the LED lights are not monochromatic. While all three of these factors suggest corrections from non-linearity, the overall deviation from the Beer-Lambert law is not very significant. However, following what is commonly done with standard spectrophotometers, instrumentation adjustments can be made to improve the calibration. Based on literature methods to correct for Gaussian beam distributions and polychromatic incident light, a power law fit can be used to correct for non-linearity with the Beer-Lambert law. It was determined that the sum of squares of the residuals is decreased when the measured absorbance is adjusted by $A^{1.033}$, using a power-law fit.

The notable advantage of the optical caustic system for measuring high absorbance is due to increased light intensity within the sample as well as a focused beam reaching the photodetector due to refraction [9]. Deviations from the Beer Lambert Law due to stray light seen at high FD & C Blue Dye #1 concentrations were not observed at the concentrations measured (Fig. 2). In fact, no special measures were taken to enclose the system nor were there adjustments made in the laboratory lighting. The photodetector housing was sufficient

to shield the detector from stray light and the caustic focus intensity was adequate for accurate recording.

3.3 Tartrazine

In order to compare the system measurement capabilities with analytes that absorb light at shorter wavelengths, tartrazine solutions were measured at 430 nm (Figs. 4 and 5). The spectrophotometer results in Fig. 4 again illustrate stray light deviation from the Beer Lambert Law at Absorbance values greater than 1. In Fig. 5, using a blue photodiode and matched photodetector, the optical caustic system gave a wider relatively linear concentration range. Interestingly, a significant deviation from linearity is seen at absorbance values greater than 1 in the optical caustic device for this setup, which was at first surprising given the results with Blue Dye #1. However, after close examination, a green light was visually observed exiting the drop at the caustic focus for concentrations greater than 0.1 mM tartrazine (Fig. 5 insert). This observation and subsequent investigation using the diffraction grating from the spectrophotometer confirmed that the light collected by the photodiode at concentrations above 0.1 mM tartrazine was essentially due to fluorescence emission.

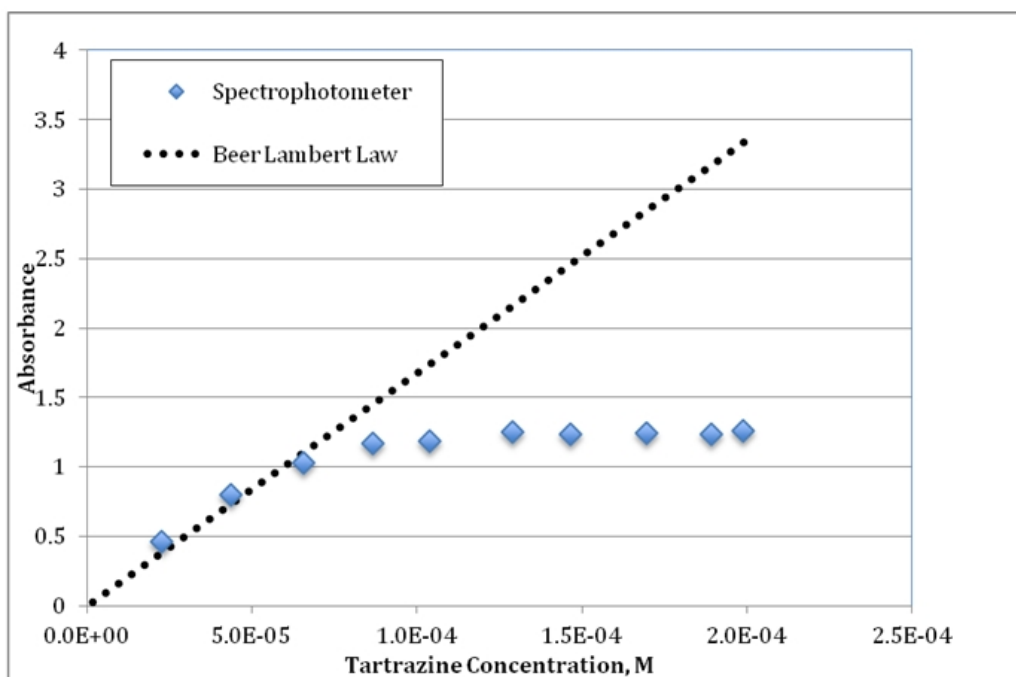


Fig. 4. Tartrazine (Yellow Dye #5) absorbance versus concentration measured at the absorbance maximum using a spectrophotometer and a rectangular cuvette. Deviation from Beer-Lambert law is seen at absorbance above 1

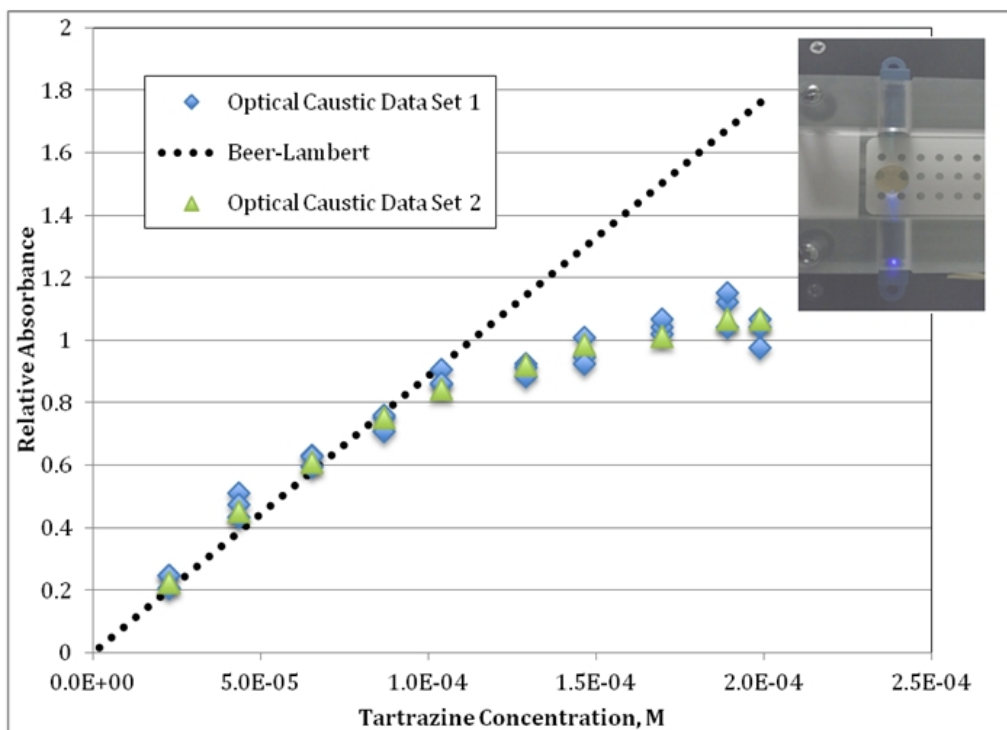


Fig. 5. Measurement of absorbance and fluorescence emission for tartrazine for the optical caustic system. Absorbance follows a linear dependence until a value of 0.8 is reached. The deviation from the Beer-Lambert law is due to the significant emission of fluorescence at concentrations above 0.1 mM tartrazine. The inset shows the fluorescent emission (green ray at the top) leaving the tartrazine solution (blue LED light excitation at the bottom). The circular wells are 3.0 mm in diameter and from the top view, the 120 microliter oblate spheroid has a major axis of 5.15 mm, measured using ImageJ, and hence a minor axis of 3.4 mm. The ellipse for ray tracing has the ratio of major to minor axis of: $b/a = 1.5$, which was confirmed by imaging the side view of water and dye solution drops

Using the UV and VIS sources in the spectrophotometer, it was observed that the intensity of light from both sources were too low to generate fluorescence even at the highest concentration of tartrazine measured. Fig. 6 shows the UV/VIS spectra for the concentrations measured in the optical caustic system, and it exhibits a shape in general agreement with published literature measurements [8].

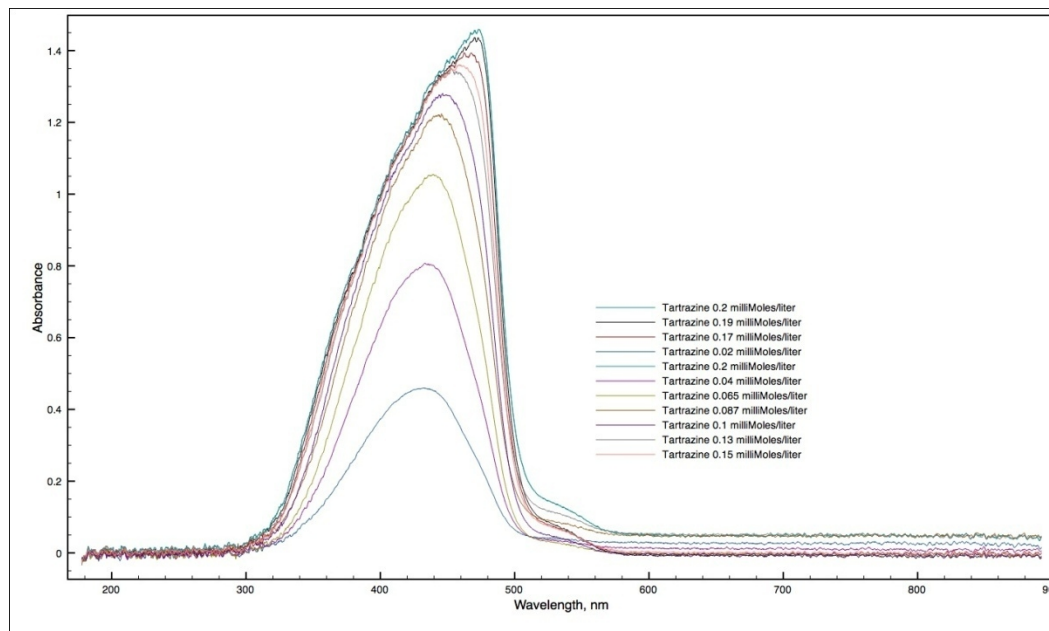


Fig. 6. Absorbance spectra for 10 concentrations of tartrazine using a spectrophotometer and a quartz cuvette. Fluorescence is not detected due to the light used for illuminating at the UV wavelengths being of too low intensity

Figs. 7 and 8 demonstrate that the optical caustic intensification of light within the sample can generate a steady state, fluorescence emission from the sample. In Fig. 7, a Blue LED is used as a light source and the diffraction grating from the spectrometer was employed to measure the intensity of light transmitted through a quartz cuvette with 0.2 mM tartrazine. No fluorescence is detected with the quartz cuvette, but a small decrease in transmitted light is detectable. However, when the sample is shaped into a spheroid using the optical caustic platform, fluorescence emission is clearly detected at a concentration of 0.2 mM tartrazine (Fig. 8). Fig. 8 shows that the transmission spectra of light exiting a 0.2 mM tartrazine solution illuminated by the red LED is not shifted, but a significant shift is seen with the Blue LED light. Since fluorescence is proportional to the concentration of the fluorescent molecule and the light intensity, it appears that the optical caustic system achieves a sufficient intensity within the sample to generate fluorescence and the emitted light does not appear to be absorbed by the solution. This is a curious result since often steady-state fluorescence spectra are generally mixed with the excitation light spectra. The steady-state fluorescence was not observed to diminish even after irradiation for 20 minutes. In Part II of the 3 part series of papers, fluorescence is explored in more detail with other fluorophores and a simple method for recording fluorescence is described.

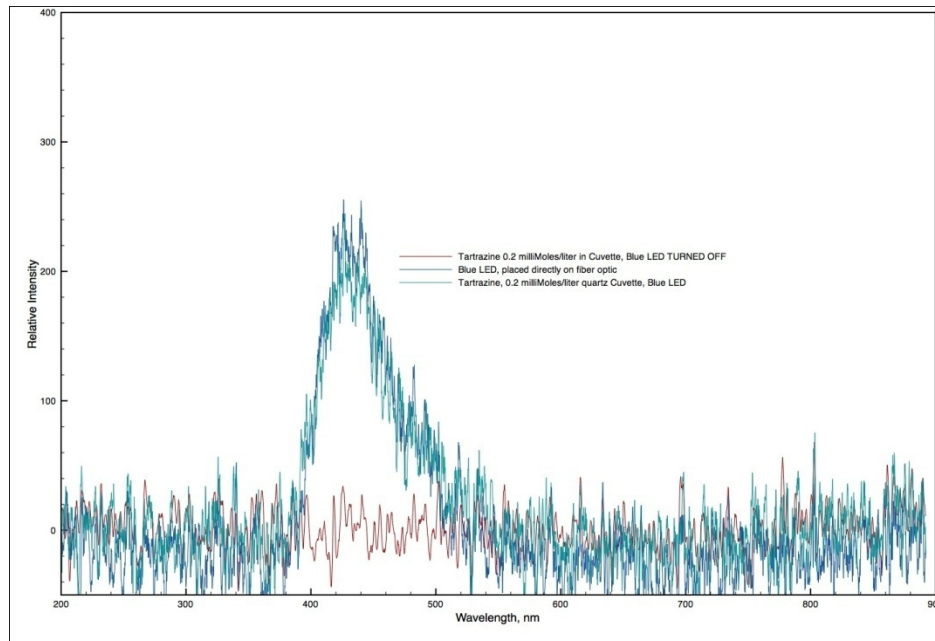


Fig. 7. Transmission spectra recorded on the spectrophotometer with the Blue LED as the light source. The blue line is the transmission spectra recorded by placing the Blue LED in front of the fiber leading to the diffraction grating. For a solution of 0.2 mM tartrazine in a cuvette, the red line is the transmission reading when the Blue LED is off and the green line is the spectra when the light is turned on.

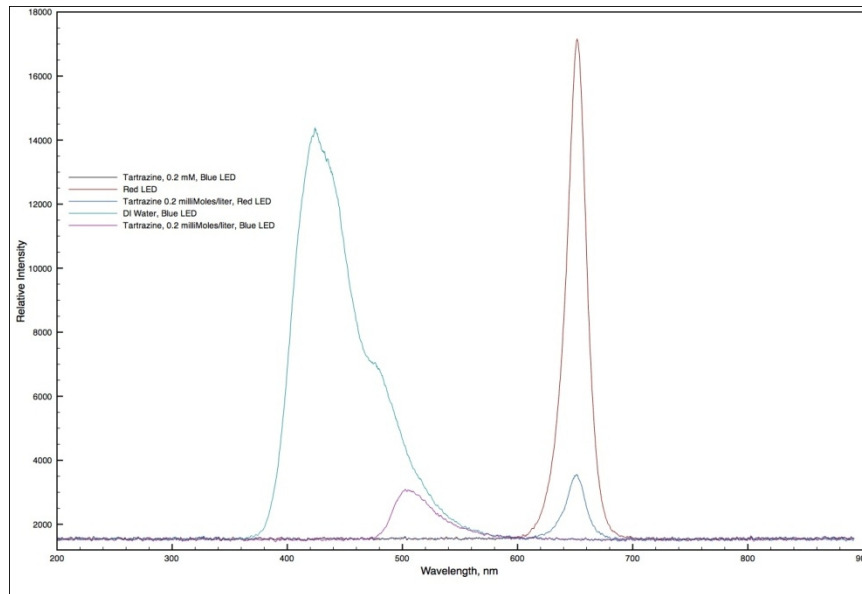


Fig. 8. Transmission spectra shown in this Figure were recorded using the spectrometer diffraction grating for the optical caustic system. Spectra for Blue and Red LED used are shown as the blue and red lines respectively. The data for tartrazine at 0.2 mM transmission spectra for oblate spheroid samples using the Blue and Red LEDs are given as the purple and blue lines respectively

4. CONCLUSION

Newton's zero order caustic can be used to measure the absorbance of solutes in a liquid sample that is in a curved spheroid shape to refract light, generating a caustic cusp of revolution and an axial spike caustic. As a result, a lower power source of light can be used to determine light absorbance. For concentration measurement purposes, a small deviation from the Beer-Lambert law is observed. For instrumentation purposes, the correction factor can be accommodated by a power-law adjustment to the measured absorbance; a correction whose basis is similar to currently practiced instrumentation corrections for light source deviations from the ideal. The dynamic range for measurement in the Newton zero order caustic is relatively high because the focusing of light within the sample extends the upper range of absorbance, whereas stray light would cause deviation from the Beer-Lambert law in standard cuvette-based systems. To analyze fluorescent solutes using light near the excitation wavelength range, very low intensity light would be needed. On the other hand, this feature could potentially be useful in detecting fluorescent solutes from a complex solution.

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COMPETING INTERESTS

Authors declare that no competing interests exist.

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