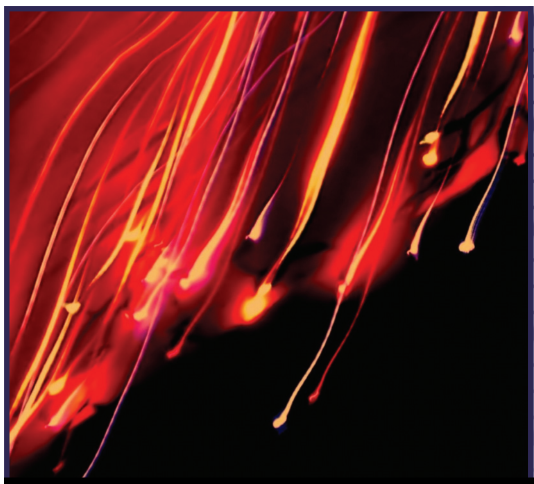

A Study of Qunizarin (Orange Dye 2) in Hexane as a Model Fuel Dye

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A study was performed using Quinizarin 1,4-Dihydroxyanthraquinone (Direct Orange 26) in hexane to model the behavior of a fuel dye. A stock of the dye solution was made and diluted before measuring the full visible spectrum (400-700 nm). The peak Absorption wavelength, found at 460 nm, had a good correlation with the Beer-Lambert Law. Additionally, the area under the Absorption profile, from 400 nm to 550 nm, was measured and also yielded an excellent correlation to the Direct Orange 26 dye concentration. Using both of the methods, the Beer-Lambert Law for the peak Absorption, and the area under the profile, one can obtain exceptional correlations of concentration and identification of the specific dye.

General

Dyes have been used to "tag" fuels for identification, concentration, environmental, and taxation purposes1-9. Most applications include marine, aviation, heating, and automobile fuels including gasoline, diesel, and kerosene. The color may vary from red, green, blue, orange, and yellow, and can be identified by the user. An example7 is the dyeing of diesel fuel, started in the United States in 1993 under Environmental Protection Agency (EPA) regulations and expanded for tax enforcement purposes on January 1, 1994. The diesel fuel dyeing programs served two distinct purposes: to identify fuel that did not meet the sulfur content for use in highway vehicles, and to identify Federal excise tax-exempt fuel. Taxation also plays a large role in the dyeing of fuels, with billions of dollars being evaded in taxes.9 Another example is quinizarin (Direct Orange 26) used in red diesel, along with Solvent Red 26 dye in the United Kingdom.

Materials and Equipment

The materials in the study consist of Quinizarin 1,4-Dihydroxyanthraquinone (Direct Orange 26, reagent grade, (98% pure) from Fluka Chemicals, and spectroscopy-grade hexane (99% pure) from Sigma-Aldrich chemicals. A Sartorius micro-balance that weighs to the mg quantity was used for all weighing. An i-LAB® model S560 visible spectrophotometer, calibrated previously with a Beckman UV/Vis/NIR Spec-trophotometer, was used to measure the transmission (T) of the dye solutions. Absorption values (ABS) were calculated using the conversion equation, ABS = -log (T). Round vials (glass, 25 mm diameter) from LaMotte were used as the sample cells.

Procedure

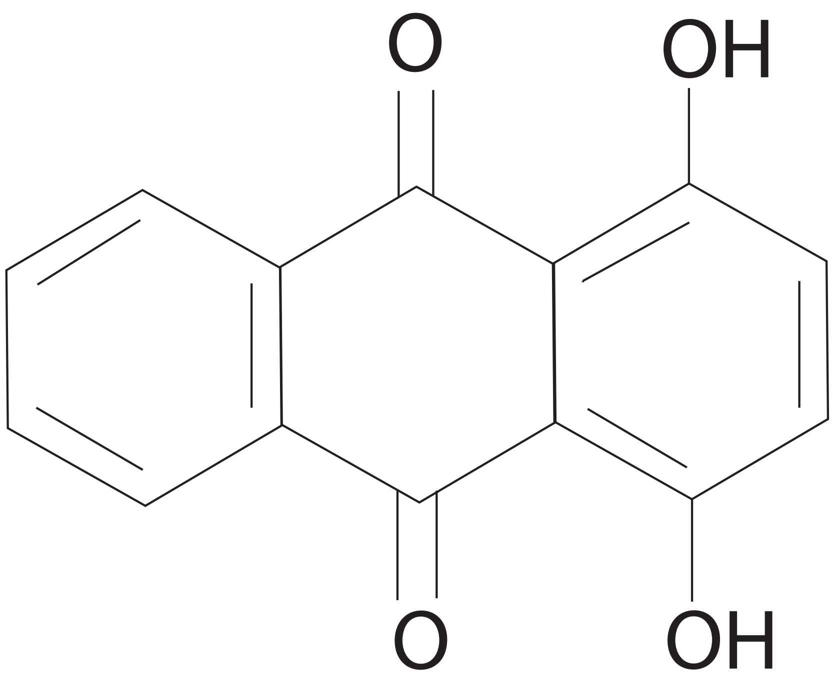

Figure 1: Direct Orange 26 Dye StructureQunizarin 1,4 Dihydroxyanthraquinone

Initially 0.100 g of the Direct Orange 26 was weighed and added to 7.500 g of hexane, forming an initial stock solution (Stock Solution A). Stock Solution A was then stirred for 30 minutes until the dye was dissolved. Another stock solution (Stock Solution C) was made by diluting 1 part of Stock Solution A with 4 parts of hexane. The prepared samples and their concentrations in micro-moles of Direct Orange 26 in ml of hexane are listed in Table 1:

Sample	Conc (umol/ml)
A	2.36E-02
B	5.89E-02
C	1.18E-01
D	1.18E-02
E	5.91E-03
F	2.95E-03

Table 1: Samples of DO 26 in Hexane

The dye solutions were placed in the 25 mm round vials and sealed, prior to measurements with an i-LAB® visible spectrophotometer. The i –LAB unit had background measurements using hexane and a black water solution, for optical purposes, before the start of sample measurement. The background measurements only needed to be performed once, and not with every sample. Each sample was measured with the LABXYZ_RV program on the unit. A typical spectrum was obtained in ~15 seconds. The data was transferred from the i-LAB unit to a computer using the DATALOG software that converting it to a Microsoft Excel spreadsheet for further analysis.

Results and Discussion

The transmission spectra of the samples are shown in Figure 2. The Transmission curves of the dye all follow the same trend. The Transmission starts at ~530 nm and continues to 700 (and probably beyond). The interesting part of the spectrum is from 400 nm to ~530 nm. The well increases in size with dye concentration, centering at ~470 nm. Figure 3 is a representation of the colors at each

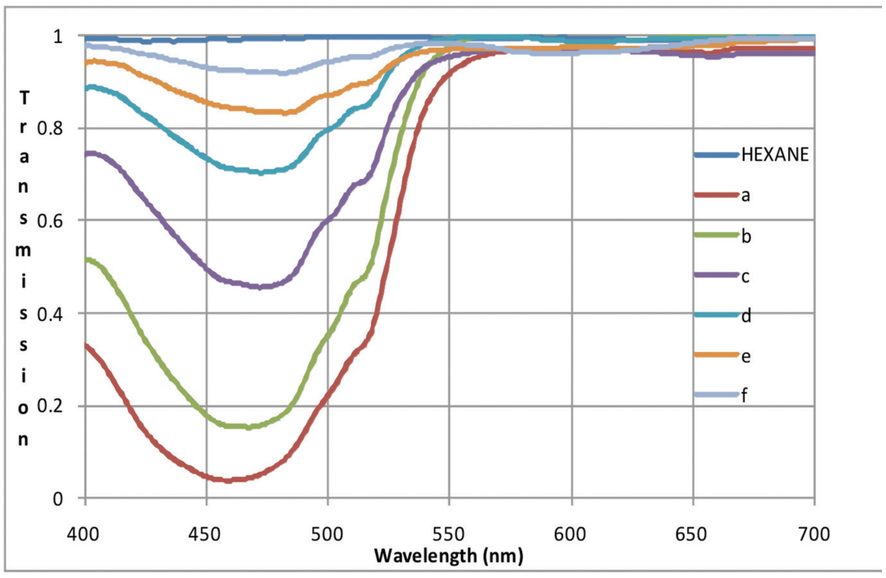

Figure 2: Transmission Spectra of Direct Orange 26 Dye in Hexane and also Hexane

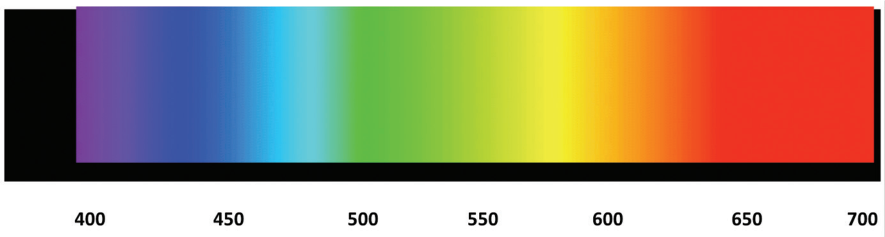

Figure 3: Color Representation of Spectra

wavelength. Figure 3 shows that the colors that are fully transmitted for the dye sample are reds and yellows, and the colors absorbed in various amounts are the blues and greens. Therefore, the sample should, and does, appear orange. As the dye concentration decreases, the color becomes paler.

Figure 4 shows the complementary Absorption spectra for the dye samples. Note that the Absorption peak gets flatter as the Direct Orange dye concentration decreases. Selecting a peak wavelength of Beer-Lambert Law could be made at 460 nm, with the blank, hexane readings being subtracted from the sample values. The Beer-Lambert plot is shown in Figure 5.

Figure 5 shows a good correlation (R2 >0.99) for a straight line fit, with the greatest variance being in the middle of the line. Practically, one could just use a spectrophotometer to obtain the peak and then use a Beer-Lambert Law to calculate a concentration. However, one could add another orange dye or a combination of dyes (i.e., yellow and red) to also get a linear correlation at the desired wavelength, in this case 460 nm. To ensure that the correct dye, as well as concentration is used, one can do a peak ratio or an area under the curve calculation. A peak ratio method involves taking the Absorbance values at two wavelengths and dividing one by the other. In the case of Figure 6, the peaks used are at 450 nm and at 500 nm. The correlation is roughly 90%, R2=0.90, with potential errors attributed to the "peaks" being taken on the actual "shoulders" of the Absorption profile. Another way to ensure the correct dye is being used is to take an area under the curve and relate that to concentration. The area under a curve method takes out the peak ratio errors of having sensitive readings on the shoulders. In this case, the Absorbance values from 400 nm to 550 nm (less hexane background) were added and plotted against the concentration of the corresponding Direct Orange 26 dye. An exponential fit has an excellent correlation (R2=0.9996) in Figure 7.

Summary

A model system for fuel dyes was made by using Direct Orange 26 dye (Quinizarin or 1,4-Dihydroxyanthraquinone) with hexane. The results show the Beer-Lambert method may be used to determine the dye concentration at 460 nm. The Direct Orange 26 dye also exhibits a unique "fingerprint" over the visible spectrum that may be determined by using a peak ratio analysis, performed here at 450 nm and 500nm, or an even better correlation using the area under the Absorption curve-from 400 nm to 550 nm for this dye. Used to its full potential, the i-LAB® visible spectrophotometer may be used to rapidly obtain outstanding dye concentration and identification for fuels and other non-aqueous solvents.

References:

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2. ASTM D156, Saybolt Color of Petroleum Products (Saybolt Chromometer Method)
3. ASTM D 1500, Test for ASTM Color of Petroleum Products (Lubricating Oil)
4. ASTM 1209, Color of Clear Liquids (Platinum-Cobalt Scale)
5. ASTM D5386, Color of Liquids using Tristimulus Values
6. ASTM D 6045, Color of Petroleum Products by the Automatic Tristimulus Method
7. Revenue Enhancement Through Increased Motor Fuel Tax Enforcement, Stephen J. Baluch, Program Manager, Fuel Tax Evasion Program, U.S. Department of Transportation-Federal Highway Administration; Presented at the Annual Meeting of the Transportation Research Board, Washington, D.C., January 1996
8. Study of the Feasibility and Desirability of Using Motor Fuel Dyes and Markers, Federal Highway Administration, Report FHWA-PL-93-022, U.S. Department of Transportation, 1993
9. National Cooperative Highway Research Program, Report 623, Identifying and Quantifying Rates of State Motor Fuel Tax Exemption, Transportation Research Board, Washington, D.C., 2008

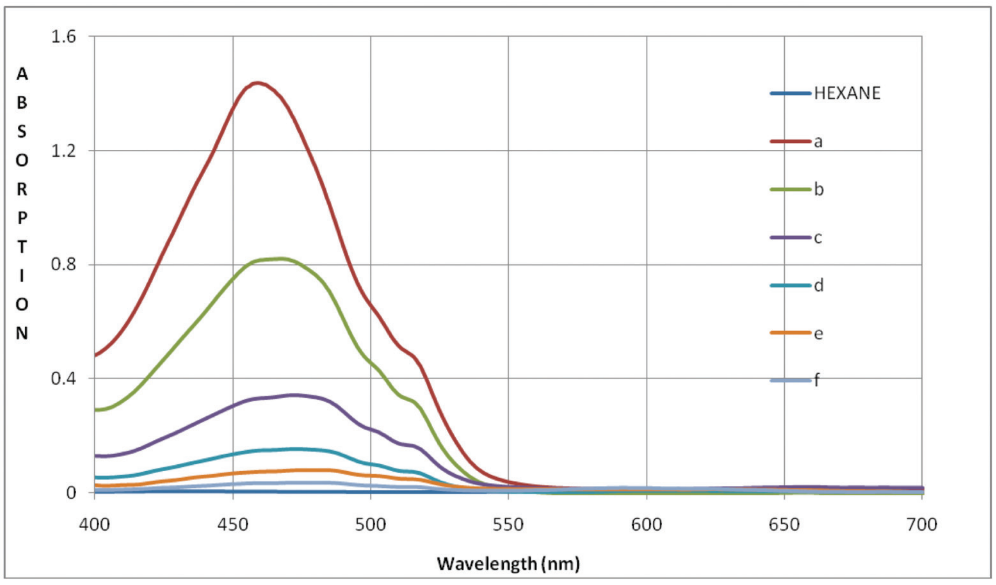

Figure 4: Absorption Spectra of Direct Orange 26 Dye in Hexane and also Hexane

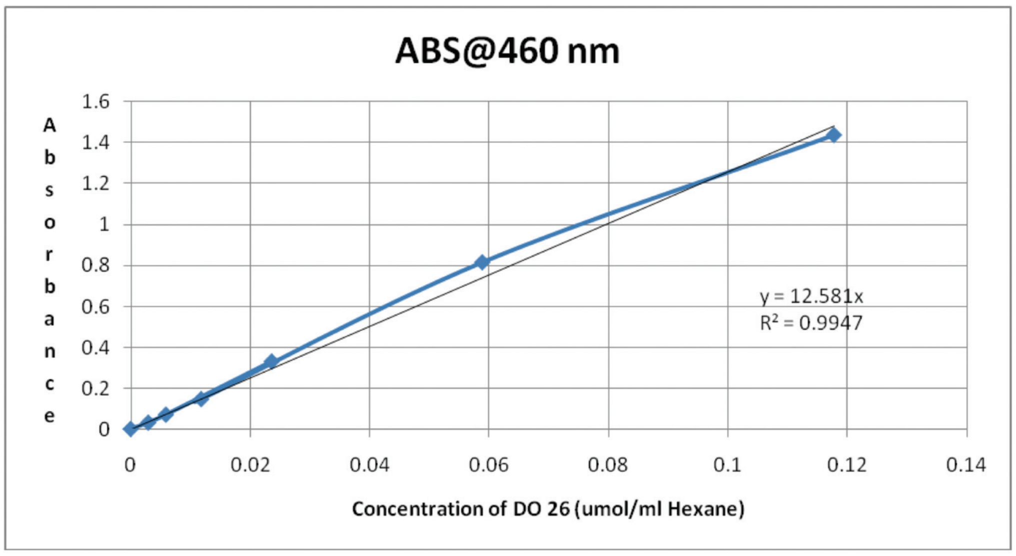

Figure 5: Beer-Lambert Plot of Direct Orange 26 Dye in Hexane at 460 nm

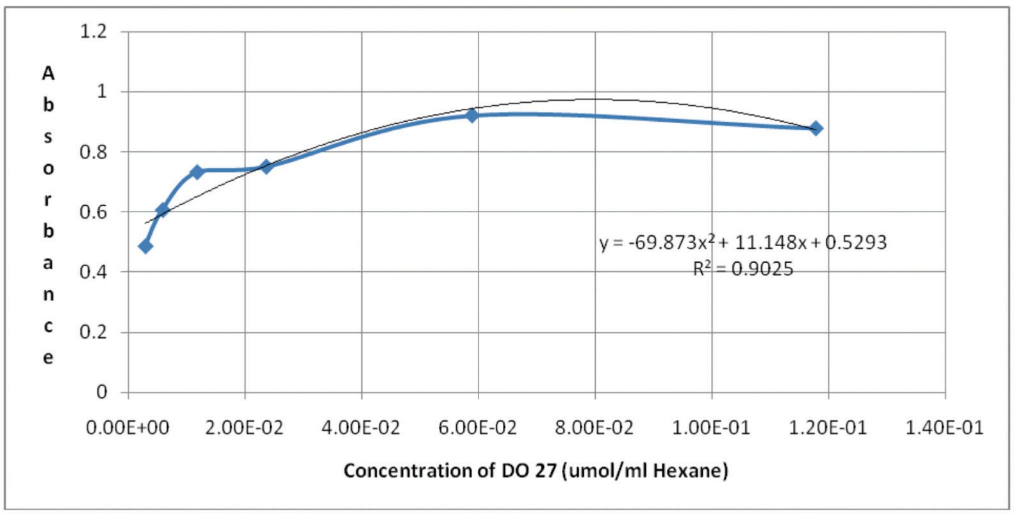

Figure 6: Peak Ratio of ABS at 450 nm/ABS at 500. Correlation is for an exponential fit

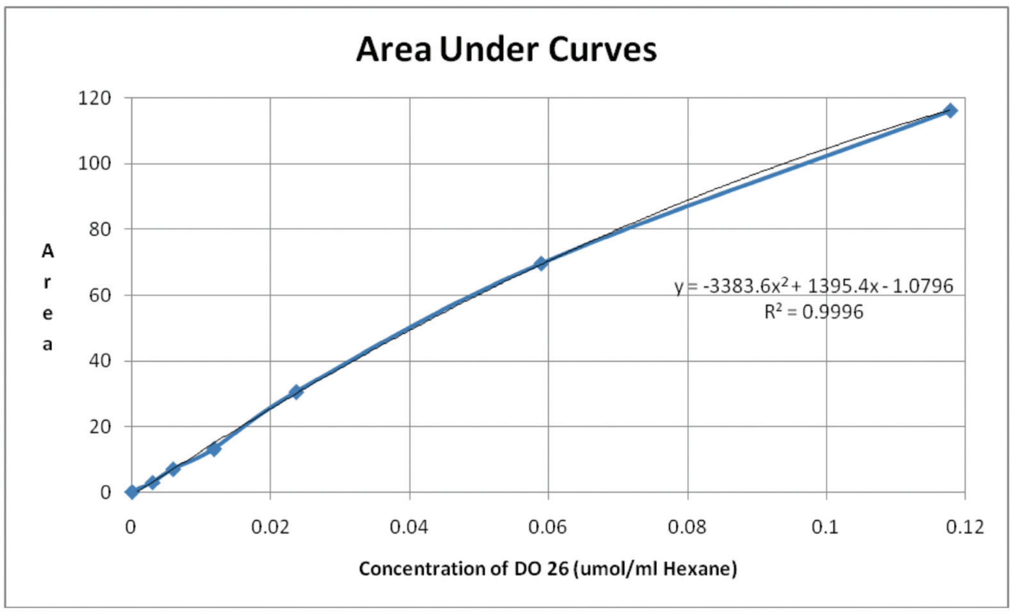

Figure 7: Area Under the Curves for ABS from 400 nm to 550 nm. Correlation is for an exponential fit