



# LUND UNIVERSITY

## Study of Fluorescence Dyes for Tracing Lubrication Oil inside Marine Engines

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Thesis submitted for the degree of Bachelor of Science  
Project duration: 10 weeks

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December 2016

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January 2017  
Lund Reports on Combustion Physics, LRCP-205  
ISNR LUTFD2/TFC-205-SE  
ISSN 1102-8718  
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# ABSTRACT

Engine lubrication is very important for engine sustainability and efficiency. It becomes even more important when heavier fuel types who contributes to lubrication are changed to alternative fuel without the same lubrication abilities. Because the performance of lubrication systems sometimes can be very hard to study in real time due to hostile environments inside engines, specialized techniques are required to improve in situ measurements.

This thesis aims to evaluate different fluorescence dye use in LIF (Laser induced fluorescence) to trace lubricant oil inside marine engines. The application of the findings could lead to a better understanding of lubrication oil distribution and possible lubrication system improvements. To conduct the tracing, the fluorescence dye must have a strong quantum yield, be compatible with temperatures normal for a marine engine liner and perturb the lubricant oils characteristics as little as possible.

Seven different dyes were studied over a temperature range normal to marine engine liners using a Nd-YAG laser to determine the quantum yield and resistivity to temperature while solved in lubricant oil. The most promising dye candidate was then used for 2D-imaging by a ICCD camera to further evaluate the tracing possibilities. The lubricant oil itself was also studied to determine its own fluorescence at wavelengths used.

The result showed that three dyes from the Pyrromethene family proved to be feasible candidates, they were soluble in the lubricant oil (Energol CL-DX 405) and had sufficient quantum yield over the specified temperature region. The most promising dye was Pyrromethene 650 due to its red shifted fluorescence spectrum that enabled suppression of the lubricant oil's fluorescence spectrum through spectral filtering.

## **ACKNOWLEDGMENTS**

I wish to thank my supervisor and friend Professor Mattias Richter of Combustion Physics at Lund University, for giving me this opportunity. For always being available for discussion and guidance when I ran into problems, giving me freedom and trust I will not soon forget.

I also want to thank my friend Fahed Abou Nada for helping me with struggles in the lab and boosting my self-confidence, a better friend is hard to find.

Finally, I wish to thank my parents for their love, endless support and understanding.

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# INTRODUCTION

The interest for increased use of sustainable and environment-friendly fuels is on a steady rise in most fields of combustion, and certain criteria concerning pollution need to be taken into account when performing any kind of combustion process.

Nowadays, large ships have to choose their fuel depending on where they want to traverse on the sea, local restrictions may limit the use of certain fuel such as Heavy Fuel Oil, which contains a great number of chemical species, such as sulfur, that are harmful to ecosystems in nature. Therefore, marine engine manufacturers and companies are in search of ways to make lighter forms of oil or alternative fuels available for use instead. However, the application of lighter oil, alcohols and gases in engines comes with a variety of side effects, such as the reduced lubrication of the engine system. Normally, the Heavy Fuel Oil used would assist in lubricating the system as it runs. However, when the fuel is changed to a lighter form, the lubrication of the fuel itself goes away and the existence of an external lubrication system now becomes even more important. Consequently, the efficiency of the lubrication system, and more specifically, the distribution of the lubricant inside the engine, becomes of high importance. One wants to be sure that the lubricant oil reaches all the important and needed sites inside the engine.

This can be studied using a variation of LIF (Laser induced fluorescence) technique that revolves around shining laser light inside the engine to receive back an emission signal from an excited fluorescence dye that has been added to the lubrication oil. This received signal will then tell us about the current position of the lubricant oil and the sites it reaches. Furthermore, the use of LIF has some benefits as a detection technique, such as the ability to measure non-intrusively while the engine is running, enabling a realistic measurement environment. The reason for applying the fluorescence dye to only new oil coming into the system is to be able to monitor its injection together with its dispersion and mixing with the oil already present inside the engine.

However, to receive a strong LIF signal from inside the engine, a fluorescence dye that is soluble in the lubrication oil and has high quantum yield is key. Further, as temperatures are varying and the oil is placed into a harsh environment, the fluorescence dye needs to be selected with care and with specific qualities in mind, such as a strong and temperature independent emission signal. This thesis aims at identifying applicable fluorescence dyes for use in LIF measurements in a marine liner engine, making sure that the needed intensity of the LIF signal and the temperature resistivity of the dye is achieved to properly determine the position and distribution of the lubrication oil in real engine measurements.

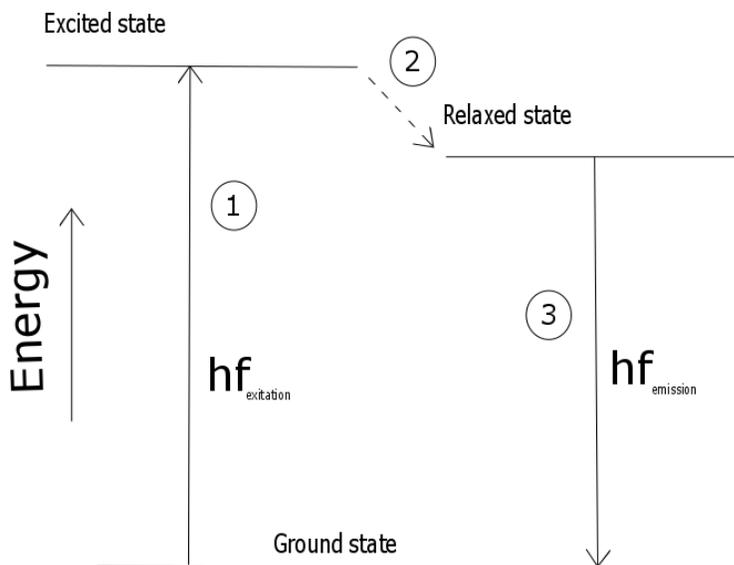
Several potential dye candidates are chosen based on previous research in the field. These dyes are then evaluated in a laboratory environment using a Class IV laser, Nd-YAG frequency doubled (532nm), for the LIF excitation process. The choice of using wavelength of 532nm was made to reduce the amount of fluorescence by the oil itself as the oil will fluorescence much more if shorter wavelengths would be used. Furthermore, the setup used means to simulate various temperatures present inside of a marine engine. The dyes, intensities and temperature resistivity are studied, after which the best candidates are chosen for their possible usefulness in 2-D imaging of oil distribution inside the engine.

# THEORETICAL BACKGROUND

## Laser-Induced Fluorescence

LIF is used in many fields of research and monitoring applications. However, in combustion physics LIF is commonly known for non-intrusively identify molecular species present in fuel and flames with the help of their fluorescence emission signal when they are excited by a laser. The technique itself is based on the process of fluorescence, which occurs in most types of molecules to some degree. Some molecules that exhibit exceptionally strong fluorescence are called fluorescence dyes as they can be applied to many different solvents, such as fuel or water, and some are used as gain media in dye-lasers. The availability of a variety of laser dyes, excitable by different wavelengths of light, offers the ability to build different lasers with exchangeable output wavelengths [1].

The process of fluorescence in such dyes can be schematically described by a simple model containing three consecutive main phases, shown in the simple electronic state diagram in Figure 1. The first phase regards the excitation and absorption, the second phase involves the excited state and its decay, the final third phase refers to the act of spontaneous emission.



*Figure 1* Simple schematic of the fluorescence process, where the three main fluorescence phases are numbered. Process one the act of absorption, process two the decay from an excited state and process three spontaneous emission.

### Excitation

The process that initiates the fluorescence is the excitation of the molecule by a suitable light source. In this thesis, an Nd-YAG laser was used as the excitation source, but other sources, such as flash lamps, can be used depending on the type of fluorescent dye. Further, it is important to note that excitation is not solely limited to photon absorption but can happen in

other ways such as by collisions with electrons or molecules. Laser excitation provides a superior way to select excitation both temporal and spatially. The excitation on the molecular level, process one in Figure 1, is initiated by the absorption of a photon by the molecule, from the external light source. Generally, most molecules are in their electron ground state at room temperature, thus this energy increase will move the electron up from the ground state into an excited singlet state [1-3].

There exist some limitations to excitation, such as photoionization and pre-dissociation. Pre-dissociation happens when the molecule is excited to a predissociative state and dissociate before it emits a photon. Photoionization happens when the molecule gets ionized due to the incoming radiation. Leading to a drastic change of the spectral properties of the molecule [3, 4].

### **Decay from excited state**

Once the molecule is in its excited state, the lifetime of such a state is limited to approximately 1 up to 10 nanoseconds, thus the state will soon go down into a relaxed singlet state by means of thermal vibrations, rotations and other energy dissipation processes. This is shown as process two in Figure 1. From this relaxed singlet state the fluorescence photon has the highest probability to be emitted. This behavior is described by Kasha's rule which states that poly-atomic molecules generally emit photons from the given multiplicity's lowest excited state [5].

It is important to note that not all photons absorbed by the molecule results in a fluorescence photon due to the fact that some energy may be lost in non-radiative manners, due to collisions, vibrations or other similar processes. This could lead to a great reduction or a complete removal of the electron excitation energy, this is called quenching. Quenching is very important to keep track of as it directly corresponds to the efficiency of the ration between emitted fluorescence photons and absorbed excitation photons, this efficiency is called quantum yield [1, 4].

### **Spontaneous emission**

Finally, spontaneous emission happens as the relaxed electronic state decays back down to the ground state of the electron, resulting in a fluorescence photon, process three in Figure 1. The loss of energy between the excited state and the relaxed state causes a shift in wavelength, this is referred to as the stokes shift. There are some benefits to study stoke shifted light as one can avoid the interference from the light emitted from the excitations source using filters such as long-pass or band-pass filters. If the emission wavelength would be the same as the excitation, it would be a resonance fluorescence [1, 3, 4].

## Spectrum

The emission peaks from such fluorescent dyes are spectrally broad band and have a more or less Gaussian shape, visualized in Figure 2. This is in contrast to the narrow discrete lines that are commonly found for atoms. The shape is also affected by the optical equipment as well as the solvent of the dye [3]. In case of several fluorescence processes being present at the same time one must be aware that these Gaussian shaped emission peaks can overlap with absorption peaks in some areas and induce pumping [1].

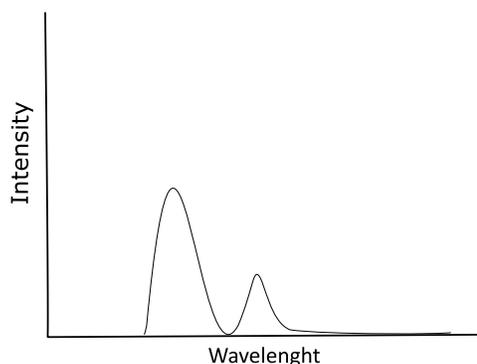


Figure 2 Visualization of broadband peaks.

## Simple LIF model

The fluorescence signal in LIF can be modeled using a simple two energy level system (Figure 3). It is important to be aware that this very simple model lacks many complex factors present in the fluorescence process, nonetheless it may serve as an approximation [3].

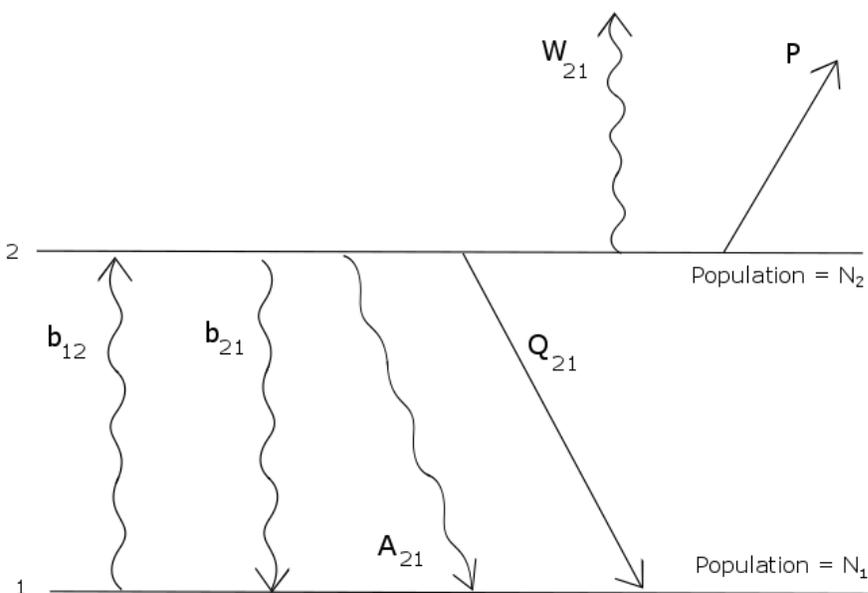


Figure 3 Shows a simple two level diagram for modeling fluorescence in LIF.  $b_{12}$  and  $b_{21}$  are rate constants for absorption and stimulated emission respectively.  $A_{21}$  is the rate constant for spontaneous emission, namely fluorescence,  $Q_{21}$  is the constant for quenching.  $W_{2i}$  is the photoionization rate constant and  $P$  is the predissociation rate constant.

The model begins with formulating the following rate equations:

$$\frac{dN_1}{dt} = N_1 = -N_1 b_{12} + N_2 (b_{21} + A_{21} + Q_{21}) \quad (\text{Equation 1})$$

$$\frac{dN_2}{dt} = N_2 = N_1 b_{12} - N_2 (b_{21} + A_{21} + Q_{21} + W_{2i}) \quad (\text{Equation 2})$$

These two equations represent the rates of population change in the two states  $N_1$  and  $N_2$ , seen in Figure 3.  $W_{2i}$  is the photoionization rate constant,  $b_{12}$  and  $b_{21}$  are rate constants for absorption and stimulated emission respectively,  $A_{21}$  the rate constant for spontaneous emission and  $Q_{21}$  the rate constant for quenching.

The above rate equations can then further be developed and used to derive an equation for the fluorescence signal (F). A simplification can be made when sufficiently low laser energy compared to the saturation energy is used (Equation 3) [3]:

$$F = \frac{h\nu}{c} \frac{\Omega}{4\pi} l A N_1^0 b_{12} I_\nu \frac{A_{21}}{A_{21} + Q_{21}} \quad (\text{Equation 3})$$

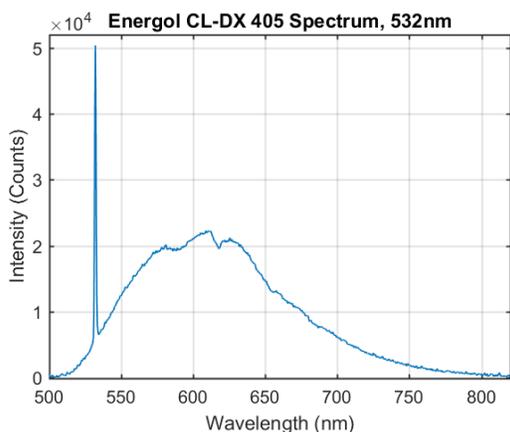
Where  $b_{12}$  is the absorption rate constant,  $A_{21}$  the rate constant for spontaneous emission and  $Q_{21}$  the rate constant for quenching,  $A$  the focal area of laser,  $l$  the length along the beam from which the fluorescence is observed,  $\Omega$  the angle of collection,  $h$  the Planck's constant and  $\nu$  the fluorescence frequency.

Equation 3 shows that quenching ( $Q_{21}$ ) play an important role in LIF signal strength. Furthermore, a linear dependence exists between fluorescence and laser energy. This equation only holds when laser energy is low compared to saturation energy [3], during the measurements, the laser energy was kept low satisfying this criterion as it helps to a deeper understanding even though it would be possible to preform the measurements at the saturated region as well.

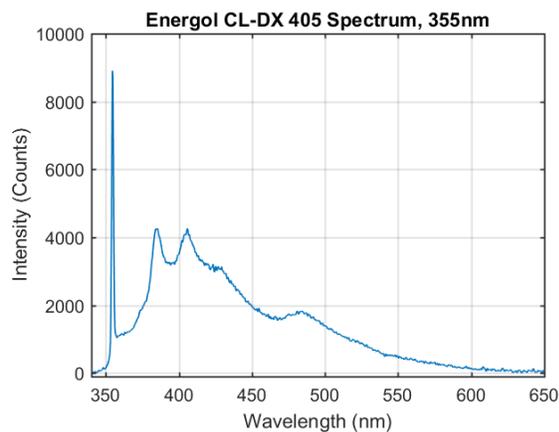
# METHOD:

## Lubrication Oil

The lubrication oil used was Energol CL-DX 405 which is a lubrication oil specially designed for use in marine engines-This oil possesses a self-ignition temperature called flash point at around 190 – 230 °C [6]. When exposed to 532 nm and 355 nm light the oil gives two distinct fluorescence spectrums (Figure 4 and 5).



*Figure 4* Emission spectrum of Energol CL-DX 40 and the visible laser peak. Excitation wavelength of 532 nm and energy at 815 J/m<sup>2</sup>.



*Figure 5* Emission spectrum of Energol CL-DX 40 and the visible laser peak. Excitation wavelength of 532 nm and energy at 66 J/m<sup>2</sup>.

## Dye selection

The selected dyes are presented below with their name, chemical formula and emission spectrum. The solvent was ethanol at minimum 93.5% purity with a water content of maximum 6.5% [7]. Where applicable the excitation was done using a frequency doubled Nd-YAG laser producing 532 nm light. However, one of the selected dyes required excitation in the UV spectral region. For this, the third harmonic at 355nm from the Nd-YAG laser was used. The laser energy used to produce the dye spectrums was not kept the same for each dye, this was done to produce clear spectrums that show cast each dye specific spectral properties without regards to any comparison between the spectrums.

The dyes were chosen due to their possibility to fulfill the needs of the experiments with regards to solubility, altering of lubricant oil properties and temperature resistance. Many of the selected dyes were selected based on previous use in similar research where engine oil were involved as the solvent for the fluorescence dye. When it comes to dyes their fluorescence emission spectra are dependent upon temperature due to the molecules being affected by thermal collisions and vibrations. If a high enough temperature is reached the fluorescence dye will stop

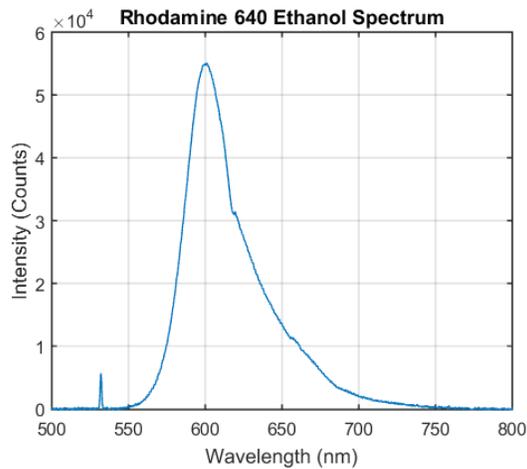
emitting fluorescence as the ground state is moved due to change of the molecular structure, this phenomenon is called thermal bleaching and needs to be avoided [1].

### **Rhodamine 640 Perchlorate ( $C_{32}H_{31}N_2O_3 \cdot ClO_4$ )**

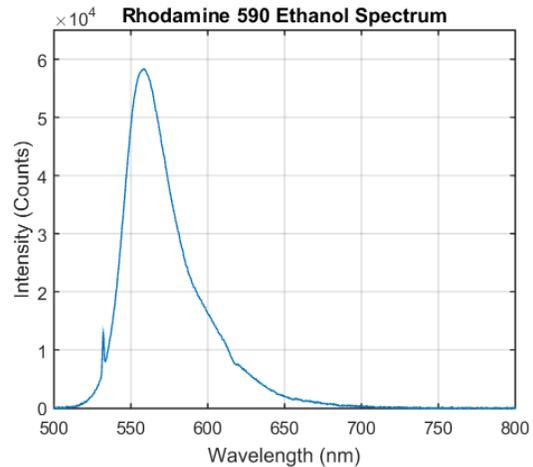
This dye is more commonly known as Rhodamine 101 and is a proficient fluorescence dye for pulsed lasers. It possesses a fluorescence peak at around 600 nm when solved in ethanol (Figure 6) and a melting point of around 210°C [1, 8, 9].

### **Rhodamine 590 ( $C_{28}H_{31}ClN_2O_3$ )**

Generally known as Rhodamine 6G this dye is one of the more well-known fluorescence dyes used with Nd-YAG 532 nm. It possesses an absorption maximum is around 530 nm when solved in ethanol [10], a fluorescence peak at around at 558 nm (Figure 7) and a melting point at around 315°C [1].



*Figure 6* Fluorescence spectrum of Rhodamine 640 when solved in ethanol. Excitation wavelength of 532 nm with laser energy at 20 J/m<sup>2</sup>



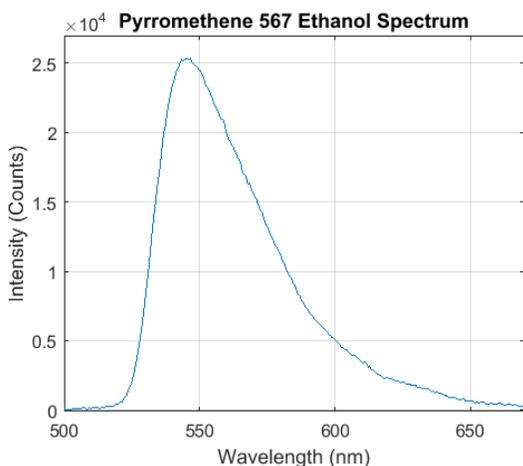
*Figure 7* Fluorescence spectrum of Pyromethene 567 when solved in ethanol. Excitation wavelength of 532 nm with laser energy at 9.2 J/m<sup>2</sup>.

### **Pyromethene 567 ( $C_{18}H_{25}BF_2N_2$ )**

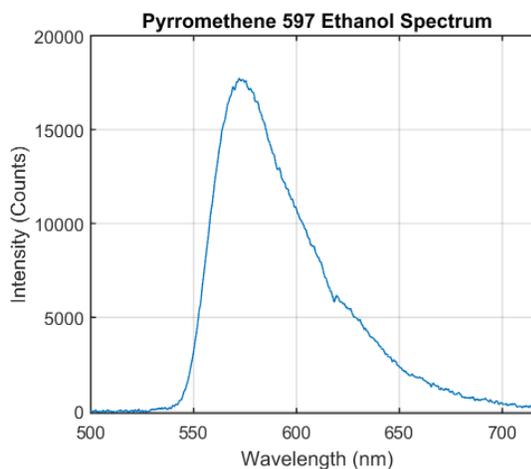
Another well-known dye, sometimes used as an alternative to Rhodamine 590 [9, 11]. It possesses an absorption maximum at around 518 nm when solved in ethanol [9], a fluorescent peak at around 544 nm (Figure 8) and a melting point at around 208-209 °C. The dye possesses a high quantum efficiency in both solid [12] and liquid solvents has been used to do oil film measurement on piston rings [1, 13-15].

### **Pyrrromethene 597 ( $C_{22}H_{33}BF_2N_3$ )**

This dye is similar to Pyrrromethene 567 but tends to have somewhat lower quantum yield efficiency due to small molecular differences, however the dye possesses a versatile solubility [11]. It possesses an absorption maximum at around 525 nm when solved in ethanol [9, 16], a fluorescent peak at around 553 nm (Figure 9) and a melting point at around 247 -261°C. The dye is soluble in many mediums such as ethanol, methanol, high temperature plastic and gasoline [1, 17-19]



*Figure 8* Fluorescence spectrum of Pyrrromethene 567 when solved in ethanol. Excitation wavelength of 532 nm with laser energy at 25 J/m<sup>2</sup>.



*Figure 9* Fluorescence spectrum of Pyrrromethene 597 when solved in ethanol. Excitation wavelength of 532 nm with laser energy at 76 J/m<sup>2</sup>.

### **Pyrrromethene 650 ( $C_{16}H_{18}BF_2N_3$ )**

Being part of the Pyrrromethene family, it exhibits similar aspects as Pyrrromethene 567 and 597. It possesses an absorption maximum at around 590 nm when solved in ethanol, a fluorescence peak with two maximums at 614 nm respectively 620 nm (Figure 10) and a melting point at around 255-258 °C [9, 20]. Additionally, an anti-stokes peak can be seen next to the laser peak in the spectrum (Figure 10).

### **DCM ( $C_{19}H_{17}N_3O$ )**

This dye possesses a broad absorption spectrum and thus absorb wavelengths all the way down to 300 nm and up to 550 nm while solved in ethanol [9, 21]. It has a fluorescence peak with two maximums at 612 nm respectively 629 nm (Figure 11) and a melting point at around 215 -220 °C [22].

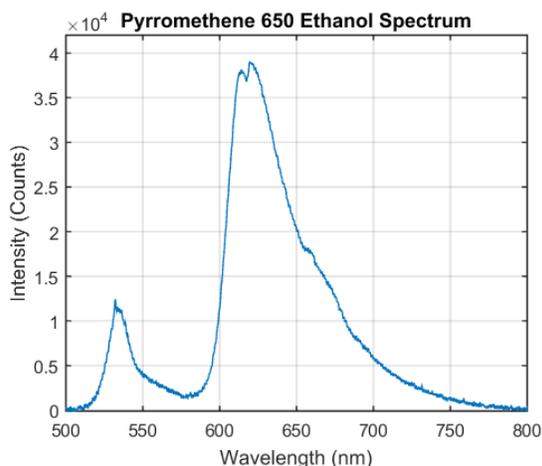


Figure 10 Fluorescence spectrum of Pyromethene 650 when solved in ethanol. Excitation wavelength of 532 nm with laser energy at  $239 \text{ J/m}^2$ .

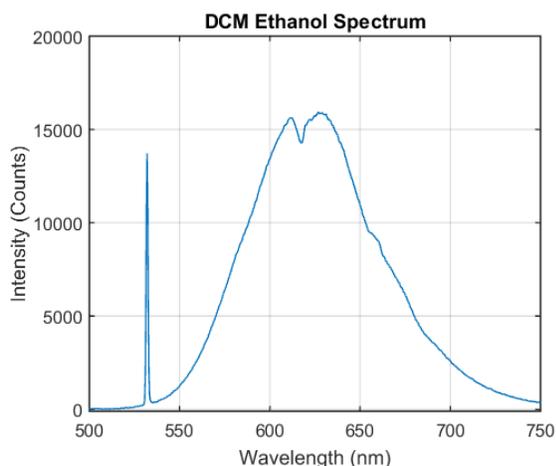


Figure 11 Fluorescence spectrum of DCM when solved in ethanol. Excitation wavelength of 532 nm with laser energy at  $66 \text{ J/m}^2$ .

### Bestoil Green FYG (NVAL)

This dye is commonly used for oil leakage detection during service and maintenance and is therefore usually excitable by handheld UV light sources. This dye could then not be excited using 532 nm and the excitation wavelength was switched to 355 nm. It has a fluorescence peak at 510 nm when solved in ethanol (Figure 12) and a melting point at  $205^\circ\text{C}$  [23].

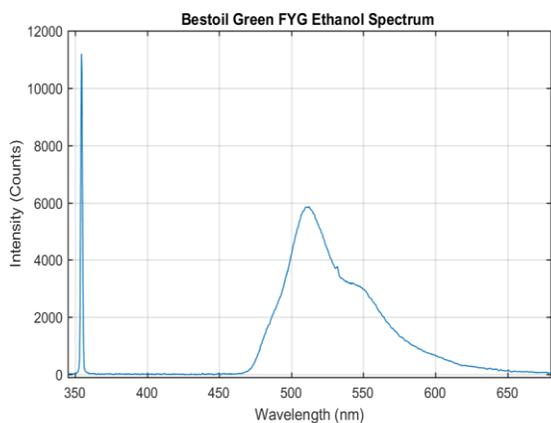


Figure 12 Fluorescence spectrum of Bestoil Green FYG when solved in ethanol, excitation wavelength of 355nm with energy of  $15 \text{ J/m}^2$ .

# EXPERIMENTAL SETUP

## Excitation Laser

The experimental setup was created with the purpose to determine the fluorescence efficiency of the individual dyes at temperatures realistic to actual marine engines. The used light source was a Q-switched Nd-YAG laser (model: Quantel Brilliant-b), which produce light at a fundamental wavelength of 1064 nm. In order to achieve the wavelengths required for excitation, the frequency was doubled to reach the second harmonic and later the third harmonic, producing light at 532 nm and 355 nm respectively. The maximum pulse energy for the two wavelengths was 300 mJ for the 532 nm and 150 mJ for the 355 nm. The fluence for the two respective pulse energies are shown in Table 1, they are calculated for an unfocused laser beam.

*Table 1:* List the used wavelengths with their respective maximum fluence, the values assumes the use of maximum laser energy for respective wavelength and an unfocused laser beam with beam diameter of 10 mm. The corrected fluence is relevant for laser safety and calculation of the laser goggle safety class, it is achieved after multiplying the fluence with a factor of  $N^{0.25}$ , where N is the number of pulses in 5 seconds, to account for the laser being pulsed.

Wavelength	Fluence	Corrected Fluence
355 nm	$1.9 \cdot 10^3 J/m^2$	$5.9 \cdot 10^3 J/m^2$
532 nm	$3.8 \cdot 10^3 J/m^2$	$10 \cdot 10^3 J/m^2$

The choice of focusing mainly on excitation by 532nm light was made mainly due to the lubricant oil generating a more intense and interfering fluorescence spectrum when excited at shorter wavelengths. However, one must be aware that other dye candidates excitable at other wavelengths might still perform the needed tracing without any complications. During the experiments the laser irradiance was measured using a power meter in short intervals during each measurement.

### Optical setup

A graphical representation of the experimental set up is shown in Figure 13. The beam path was aligned onto the sample using one dichroic mirror specified for wavelengths of 532 nm together with a quartz beam splitter. This enabled the use of higher laser output which in turn helps stabilize the beam energy. The beam-splitter used had an approximate reflection of four percent which was then used to perform the excitation of the sample, whereas the majority of the generated radiation passes through, into a dedicated beam-dump.

Thereafter the beam went through an aperture, which blocked the Gaussian wings and scattered light from the beam profile, in order to achieve a more homogenous top hat profile. The beam with a diameter of 5 mm, was then made to go through the part of the sample holder that's closest to the collection lens to avoid signal trapping of the produced fluorescence.

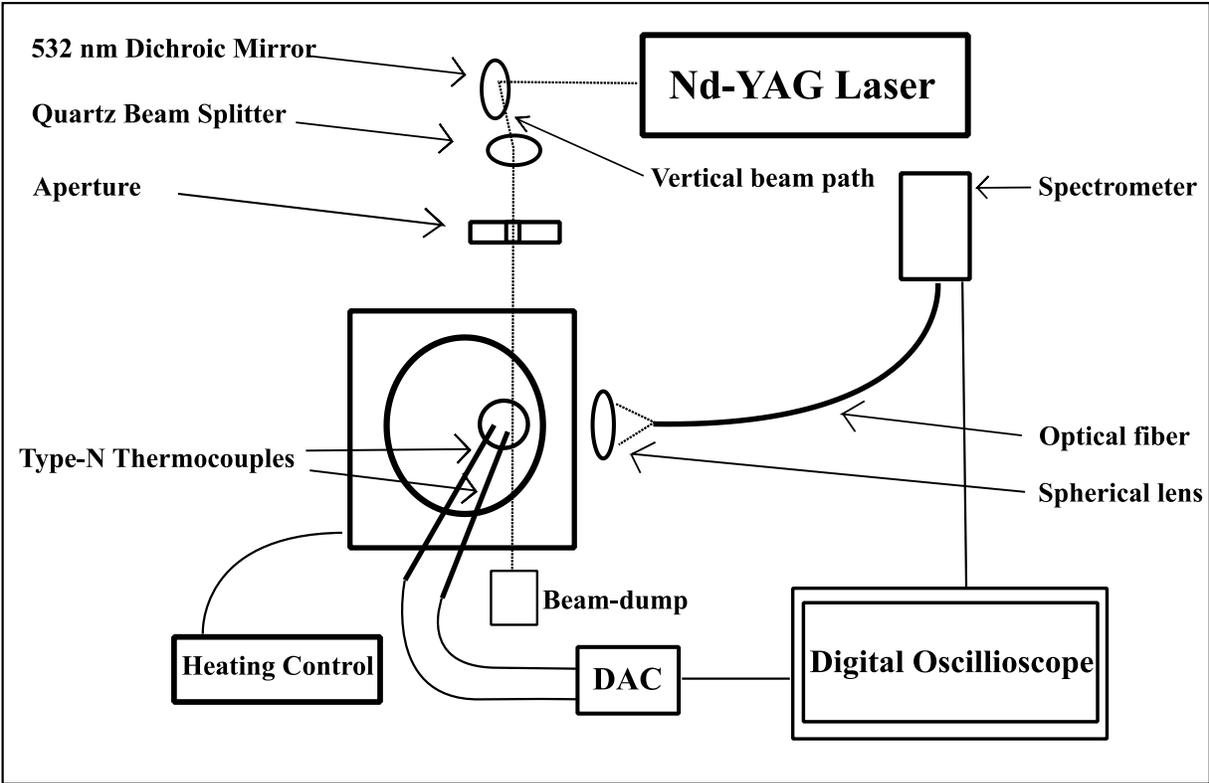


Figure 13 Schematic view of the experimental set up.

### Sample preparation and placement

Each sample was prepared in a chemical cabinet, the dye concentration was measured using a scale with a precision of 0.001 g [24] and the oil quantity was measured by marked pipettes, with a precision of approximately 0.5 ml. Thereafter the oil was heated up to 40°C in an ultrasonic bath for approximately 10 minutes to improve mixing.

During the measurement, the oil sample was kept inside an Erlenmeyer flask made of clear Duran® glass, this flask type is highly thermal resistant and possess low absorption of maximum 10 percent in the spectral range of 350 up to 2000 nm [25]. The heating of the sample was performed by a circular heating plate, able to increase the temperature of the sample to 150°C. The temperature range was chosen to cover the normal temperatures of 75-125°C in a marine engine liner.

### Signal and temperature acquisition

Using a spherical lens with a diameter of 50 mm and a focal length of 60 mm the fluorescence signal from the sample was directed onto an optical fiber cable connected to a spectrometer. The fiber was intentionally placed at a 90° angle relative to the laser beam path to minimize the amount of light from the laser reaching the spectrometer. The spectrometer had a resolution of 1.10-1.30 nm [26], the resulting spectrums were visualized on a computer.

For measuring temperature, two individual thermocouples of type N were used. The Type-N thermocouples are made out of a Nicrosil and Nisil alloy, with an approximate uncertainty of 1.5°C and a temperature maximum at 1200°C [27]. These were connected to a

DAQ card which transferred the signal to a digital oscilloscope running LabVIEW programming language. The laser energy was evaluated separately using a pyroelectric sensor without diffuser connected to a universal power meter that logged the measurements.

## 2D – Imaging set up

The imaging set up (Figure 14), reused parts of the previous setup with some small modifications. The same doubled frequency Nd-YAG laser producing 532 nm light was used and the optical alignment was done in a similar way. However, the beam splitter was replaced with another dichroic mirror and a spherical expansion lens with a focal length of -50 mm was added between the dichroic mirrors and aperture, to illuminate an area of approximate 80 cm<sup>2</sup> on the metal target. The target itself was a metal plate covered with a thin layer of lubricant oil without any tracer dye added. During the measurements, a small amount of dye traced lubricant oil was introduced and let to move over the plate. Pressurized air was later blown on the metal palatte to simulate movement in other directions.

The imaging was done using an intensified CCD camera (ICCD model: ANDOR iSTAR) triggered by the laser and coupled to an oscilloscope and computer. The studied dye was Pyrromethene 650, therefore an optical bandpass filter; centered around 589 nm with a FWHM of 10 nm and a diameter of 50mm, was placed in front of the camera.

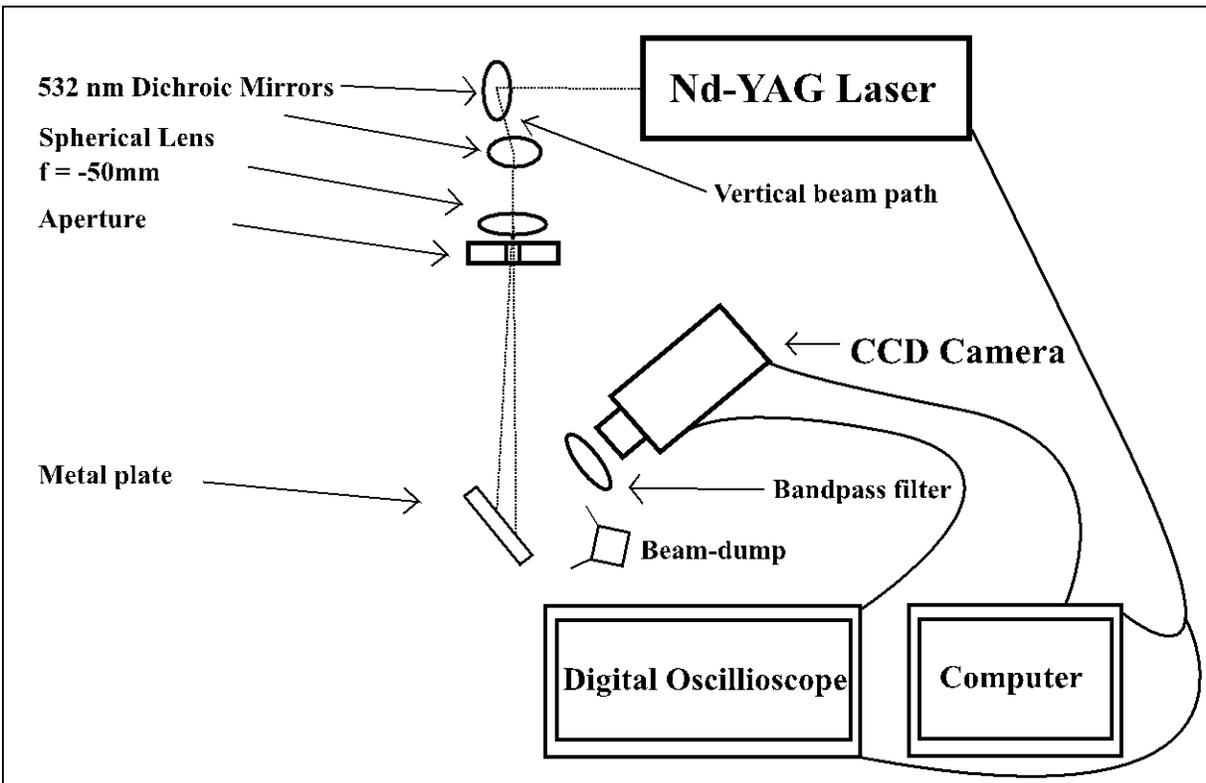


Figure 14 Schematic view of the 2D imaging setup.

# RESULT AND DISCUSSION

The goal was to evaluate different fluorescence dyes to be used to trace lubrication oil inside marine engines. The dyes should be soluble in the lubricant oil, resistant to temperatures of 75-125°C, normal for these engines and to as a small degree as possible not perturb the characteristics of the oil, therefore the concentration of the dye was kept to a minimum.

## Temperature resistance

The following results show the emission spectrums of each individual dye when solved in lubricant oil at increasing temperatures together with their temperature dependent intensity curve. Each measurement was taken during a short period were 15 spectrums recorded at the same temperature were averaged into the final one shown in the result, this procedure reduces the effect of laser fluctuations upon the measured intensity. During this time the temperature was slowly increasing but stayed well within the deviation range for the thermocouples at 1.5 °C.

### Pyrromethene 567

The spectrum of this dye lays on top of the lubricant oils own spectrum, however with a much higher intensity (Figure 15). The laser fluence was averaged around 18.8 J/m<sup>2</sup> with a dye concentration of 0.025 g/L. The dye intensity at the start of the temperature increase can be seen as a dip before a small rise, above 40 degrees the intensity decreases with increasing temperature (Figure 16).

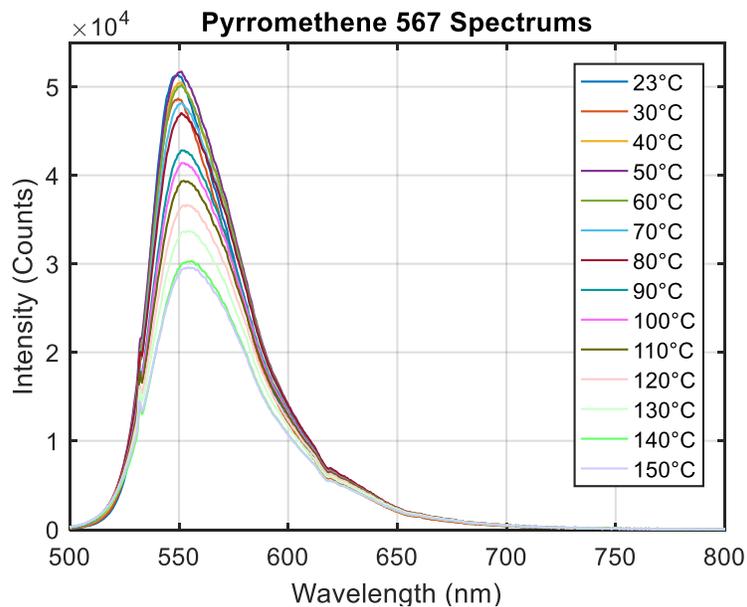


Figure 15 Spectrums of Pyrromethene 567 at different temperatures ranging from room temperature at 23°C up to 150°C.

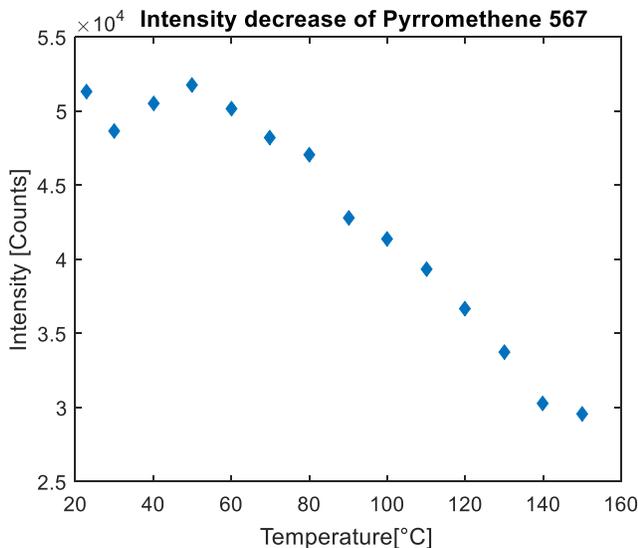


Figure 16 Pyrromethene 567 fluorescence intensity at increasing steps of lubricant oil temperatures.

Pyrromethene 567 had an almost constant decrease of intensity over the temperature range (Figure 16). The dye did however display a behavior at low temperatures, in the form of a dip followed by a small increase only to start decreasing again. This could be due to the dye behavior or it could also be a feature caused by statistical averaging of the signal peak values.

### Pyrromethene 597

The laser energy fluence was averaged around  $17.8 \text{ J/m}^2$  with a dye concentration of  $0.025 \text{ g/L}$ . The signal intensity of the dye at increasing temperatures can be seen slowly decreasing (Figure 17 and 18).

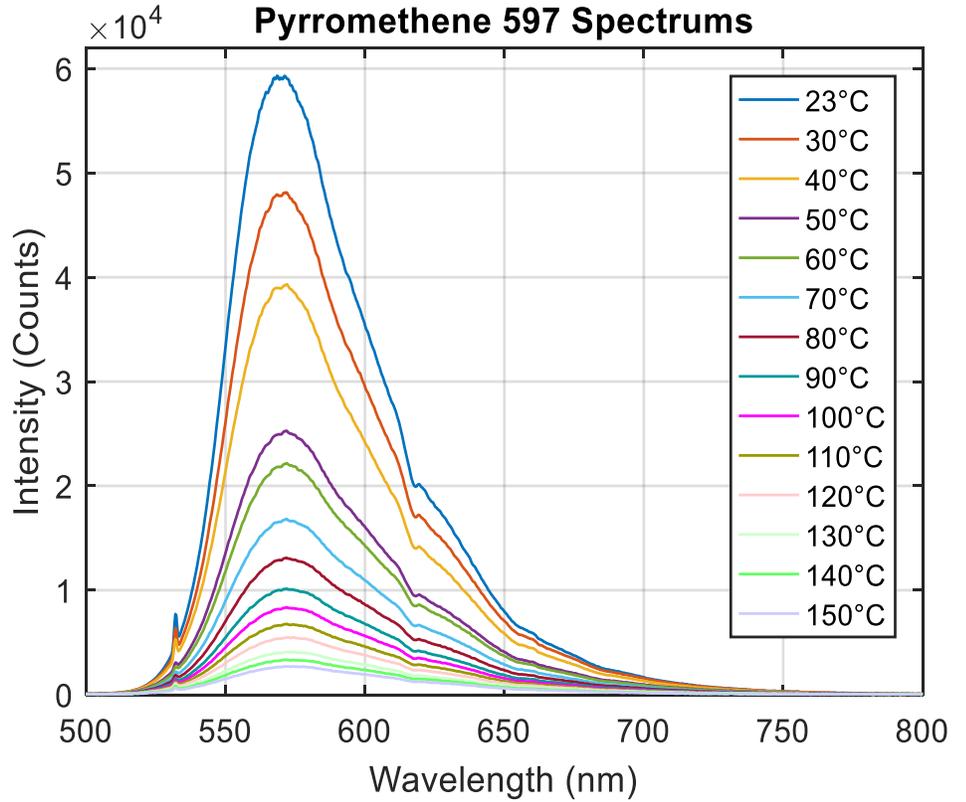


Figure 17 Spectrums of Pyrromethene 597 at different temperatures ranging from room temperature at  $23^\circ\text{C}$  up

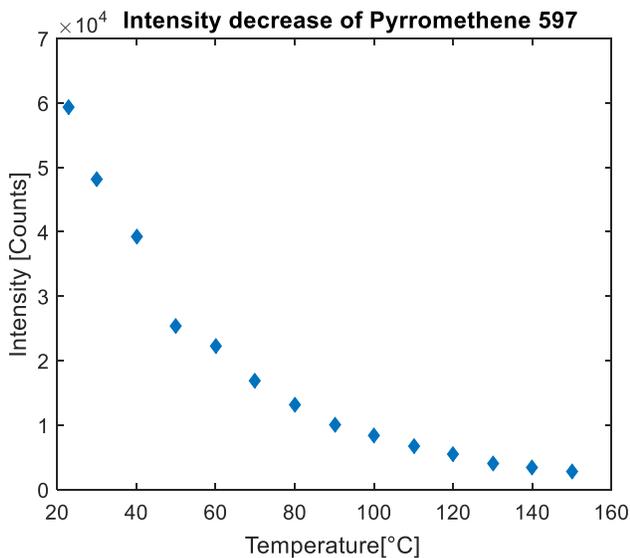


Figure 18 Pyrromethene 597 fluorescence intensity at increasing steps of lubricant oil temperatures.

All three Pyrromethene dyes proved to have a high quantum yield, requiring very low dye concentration for adequate signal. The dye Pyrromethene 597 can be seen to have a large intensity drop from  $6 \cdot 10^4$  counts down to  $0.2 \cdot 10^4$  counts over the tested temperature range (Figure 18). For Pyrromethene 567 (Figure 16) one can note a similar drop of intensity but not as drastic of  $5.2 \cdot 10^4$  counts down to  $2.9 \cdot 10^4$  counts. The intensity change due to temperature for Pyrromethene 597 seems to stabilize at higher temperatures which lessens the impact on the fluorescence signal due to temperature fluctuations located at the measuring point. This intensity decrease is expected due to thermal-quenching. Due to the low amount of laser energy used in the evaluation, it should be possible to compensate for the low intensity at higher temperatures by using higher laser energy when performing measurements in engines at a temperature above 130 degrees.

Both Pyrromethene 597 and Pyrromethene 567 also had their respective fluorescence spectrum overlapping with the lubricants oils own spectrum (Figure 17 and 15), making it hard to only measure the dye spectrum. However, both dyes produce significant more fluorescence than the oil, which makes the fluorescence ratio of dye to oil large enough for tracing use. It should also be noted that these two dyes were the easiest to solve in the lubricant oil, requiring almost no stirring or heating to be fully mixed.

### Pyrrromethene 650

The laser energy fluence was averaged around  $40.7 \text{ J/m}^2$  with a dye concentration of  $0.025 \text{ g/L}$ . The intensity of the dye at increasing temperatures can be seen as steadily decreasing (Figure 19 and 20).

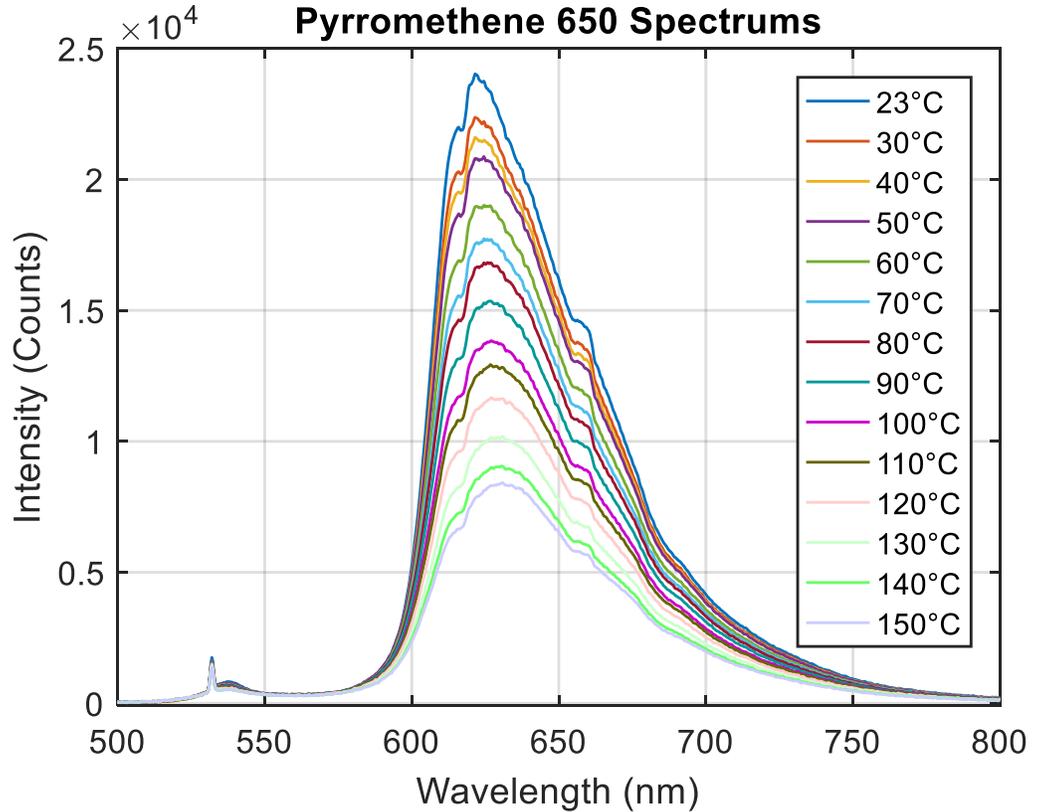


Figure 19 Spectrums of Pyrrromethene 650 at different temperatures ranging from room temperature at  $23^\circ\text{C}$  up to  $150^\circ\text{C}$ .

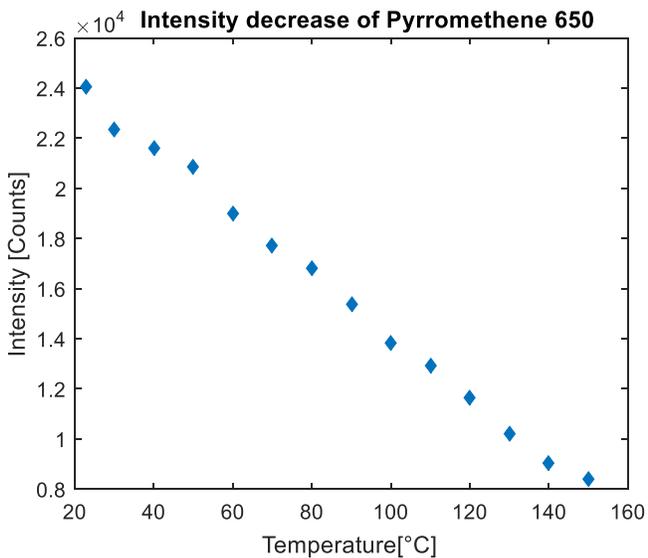


Figure 20 Pyrrromethene 650 fluorescence intensity at increasing steps of lubricant oil temperatures.

Pyrrromethene 650 had a constant decrease over the measured temperature range (Figure 20). The fluorescence spectrum was red shifted (Figure 19) compared to the other dyes which allowed for suppression of the oil fluorescence by spectral filtering. This dye had lower quantum efficiency than the other two Pyrrromethene dyes and therefore a slightly higher laser energy was

required. This dye was later selected for use in the 2D-imaging, due to the ability to filter away much of the oil fluorescence spectrum using a bandpass filter. The dye had a crystalized appearance and required more stirring than other dyes to solve in the lubricant oil.

**Bestoil Green FYG**

This dye was excited using 355 nm. The fluorescence spectrum of the dye was seen between 470 nm up to 600 nm, redshifted approximately 25 nm from the oil spectrum; stretching between 350 nm to 450 nm (Figure 21). The laser fluence was averaged around 45.8 J/m<sup>2</sup> with a dye concentration of 0.25 g/L.

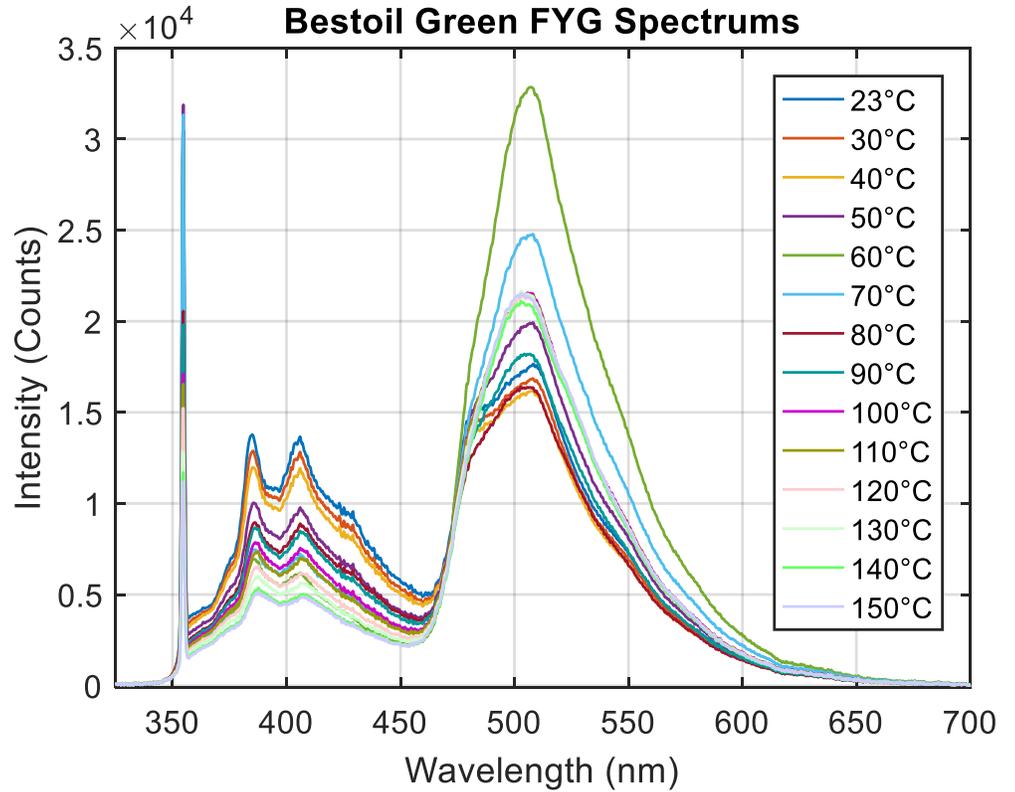


Figure 21 Spectrums of Bestoil Green FYG at different temperatures ranging from room temperature at 23°C up to 150°C.

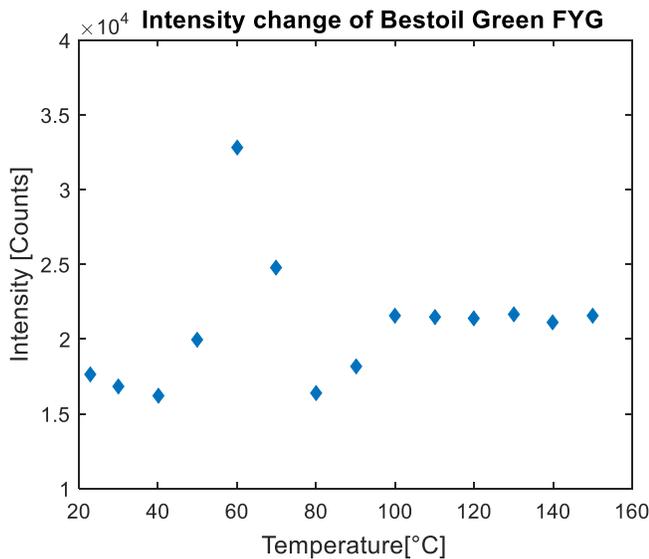


Figure 22 Bestoil Green FYG fluorescence intensity at increasing steps of lubricant oil temperatures.

The dye had a low quantum efficiency, requiring around ten times the concentration of the other dyes to achieve satisfactory signal, therefore possible presence of perturbations to the oil characteristics one cannot be excluded, such perturbations, if they exist, are unwanted. The dye spectrum can be seen red shifted enough to enable suppression of the oil fluorescence by spectral filtering (Figure 21). The dye shows a peculiar response to temperature change (Figure 22), it starts off decreasing slowly only to peak at 60°C, later stabilizing at 100°C -150°C. The behavior is similar to that of Pyrromethene 567 at low temperatures, but much more extreme.

### **Rhodamine 590**

Rhodamine 590 turned out to be not soluble in the lubricant oil used and therefore was not used in further studies. For investigation, the dye's solubility was tested in n-heptane but it proved to be un-soluble there as well.

### **Rhodamine 640**

Rhodamine 640 seemed to be soluble in the lubricant oil but yielded no signal even when exposed to laser fluence of around 1020 J/m<sup>2</sup>. This could be the result of severe quenching or un-solubility in the lubricant oil, therefore this dye was not used for further studies.

### **DCM**

DCM turned out to be not soluble in the lubricant oil and therefore was not used for further studies.

### **Acquisition**

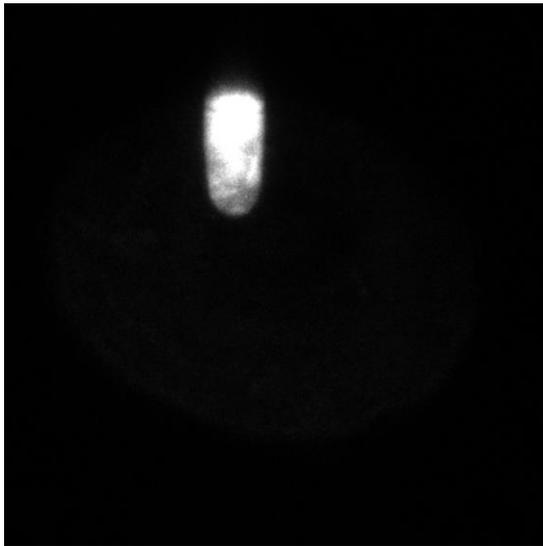
During the spectrum acquisition process, the laser energy was fluctuating from pulse to pulse, measured with a power meter. In Equation 1, we see that the fluorescence signal is linearly dependent upon the laser energy below the saturation region [3], the measurements done, are believed to be below this saturation region, as the intensity was measured to vary with changing energy. It's important to note that the results don't need to be from below the saturation region to be valid for practical use. All spectrums were acquired by averaging 15 spectrums at each temperature, averaging away much of the effect from the pulse-to-pulse energy fluctuations. When it comes to practical use, one can measure these fluctuations and compensate for them.

The uncertainties in this measurement mainly comes from the dye concentration, based upon the accuracy of the scale and pipettes used. The temperature uncertainties were determined by the thermocouple accuracy.

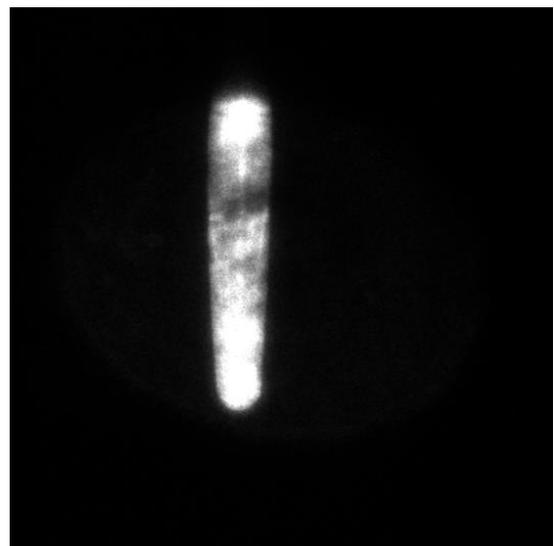
## 2D-Measurement

Pyrrromethene 650 was chosen as the tracer for the lubricant oil in this measurement, due to the dyes spectral red shift giving the ability to filter away the fluorescence spectrum of the lubricant oil. This makes easy to distinguish the traced lubricant oil from the non-traced oil.

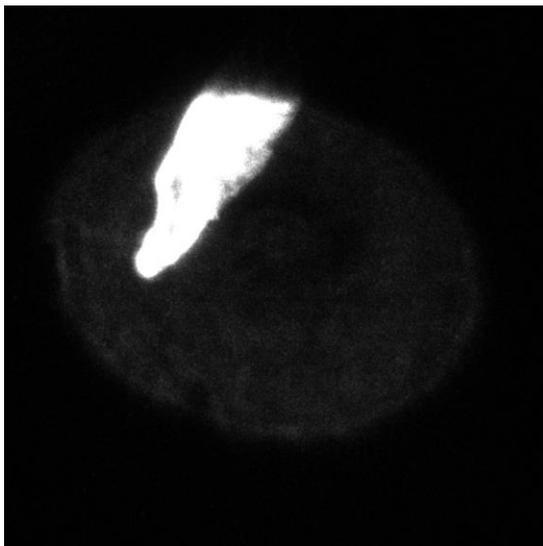
The result of the Pyrrromethene 650 traced lubricant oil by 2D imaging with an ICCD camera show the traced lubricant oil while it is moving across a metal area of  $80\text{ cm}^2$  covered in untraced lubricant oil, while illuminated by the 532 nm laser light. The fluence on the target area was then  $1.25\text{ J/m}^2$ . A bandpass filter centered around 589 nm with a FWHM of 10 nm was used to isolate the dye signal, which gave a signal to noise ratio of 10:1 of the shown figures. Figure 23 and 24 shows the oil moving by gravity across the target metal plate.



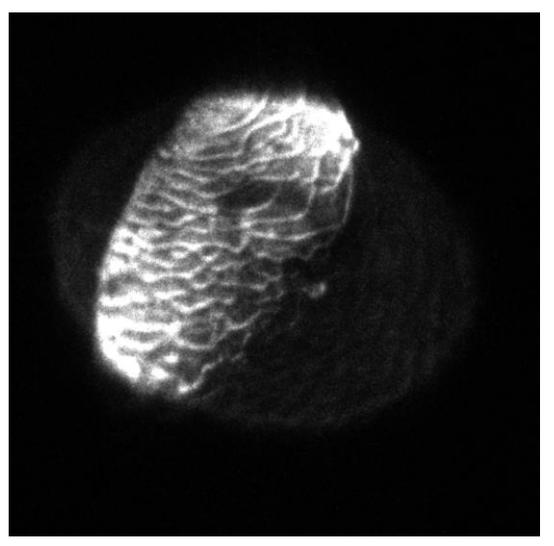
*Figure 23* Showing the Pyrrromethene 650 traced lubricant oil when introduced to the metal surface covered in un traced oil.



*Figure 24* Showing the Pyrrromethene 650 traced lubricant oil at a later strage further down the metalplate.



*Figure 25* Showing the Pyrrromethene 650 traced lubricant oil when introduced to the metal surface, now moved using pressurized air flow.



*Figure 26* Showing the Pyrrromethene 650 traced lubricant oil moved with pressurized air at a later stage, the waves caused by the air can be seen clearly.

Figure 25 and 26 shows a new traced oil sample, as it moves on the same target plate by pressurized air flow.

The bandpass filter that was used to filter away the oil spectrum limits the fluorescence output of Pyrromethene 650 (Figure 23, 24, 25 and 26). The filter, centered at 589 nm with a FWHM of 10 nm, lets through only a part of the short wavelength side of the dye's fluorescence peaks (Figure 19). The goal here is to try to simulate a harsh environment common for in suite measurements in engines, where factors, such as window fouling, will reduce the signal. One can then drastically increase the dye signal by using a filter centered at around 624 nm with a FWHM of 20 nm. The introduced traced oil was later moved around on the target plate using pressured air (Figure 25 and 26). In these figures one can see the untraced lubricant oil in the background, this is possible due to the high pulse energy used and that the filter catches the end tail of the oil fluorescence spectrum. However, this is not a problem as long as one can easily distinguish the locations with new traced oil from those with un-traced oil. Also, the choice of optical filter represents the worst-case scenario in terms of cross-talk between traced and un-traced lubricant oil.

## **Improvements**

These measurements could be complemented by moving them inside a working engine. This would allow for evaluation in hostile environment, where the oil absorption characteristics might change due to oxidation and soot contamination [1]. Further the different dyes ability to handle high pressure have not yet been studied, moving the measurement inside an engine or the use of a pressurized chamber would allow further studies of this. The temperature range was chosen to satisfy normal marine engine liner temperatures.

It would also be of interests to further investigate the solubility problem of Rhodamine 590, DCM and Rhodamine 640. Finding the explanation would make it easier to select dyes appropriate for tracing of different kinds of lubrication oils and to understand why some of these dyes have worked before in other studies [1].

## CONCLUSION AND OUTLOOK

The three evaluated Pyrromethene dyes 567, 597 and 650 proved to be valid choices for lubricant oil tracing, where the solution oil was Energol CL-DX 405. They all displayed a high quantum efficiency when excited using 532 nm light. Nonetheless, they all displayed an efficiency decrease due to increasing temperature, were the least affected was Pyrromethene 567. The Bestoil Green FYG dye would likewise suffice if excitation by 355 nm and the use of higher dye concentration proves no problem, however one must not forget about the increased fluorescence by the oil itself when excited by UV light. In the end, due to the red shift of Pyrromethene 650 fluorescence spectrum, which gives possibility to remove the oil spectrum, Pyrromethene 650 was proven to be best candidate for this type of measurement in the engine liner temperature range.

The next step of continuing this research will be to perform in situ engine measurements during 2017, to confirm the tracing efficiency, performance and evaluate pressure resistance of the dyes. The use of one of the recommended dyes could lead to good tracing of lubricant oil movement within marine engines, which is expected to lead to improvement of the lubrication system.

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