



Investigations to characterize the interactions of light radiation, engine operating media and fluorescence tracers for the use of qualitative light-induced fluorescence in engine systems

Thorsten Schweizer¹ · Heiko Kubach¹ · Thomas Koch¹

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Abstract

The light-induced fluorescence (LIF) represents an important tool for the continuous improvement and further development of combustion engine systems regarding efficiency increase. In this work, the interactions between light-emitting diode (LED) and laser diode light radiation, engine oil/fuel and three fluorescence tracers are investigated on an application-related investigation system for the design of qualitative LIF experiments. Thereby two efficient light sources for engine combustion chamber lighting are presented. For different engine oil/fuel tracer combinations, the fluorescence is examined in its intensity and its spectrum depending on the temperature, concentration and temperature history. With oil temperature variations of up to 150 °C, changes in the fluorescence spectrum and fluorescence intensities that decrease by up to 80% are evident. For specific tracer oil/fuel mixtures, concentration-dependent maximum intensities and different temperature history behaviors can be revealed. The results shown support the design of spectral engine examination setups and give tracer dosage recommendations. Additionally, an engine LIF setup for in-cylinder tracking of engine operating media is presented.

Keywords Light-induced fluorescence · Engine combustion Chamber lighting · Concentration/temperature characterization · Doped engine operating media · Engine LIF setup

Abbreviations

LIF	Light-induced fluorescence
LED	Light-emitting diode
SPF	Short-pass filter
PM567A	Pyromethene 567A
LSPI	Low-speed pre-ignition
PID	Proportional-integral-derivative
RPM	Revolutions per minute
BMEP	Brake mean effective pressure
SP-F	Short pass filter
LP-F	Longpass filter

1 Introduction

On the way to climate-neutral mobility, the increasingly complex development and improvement of engine systems are of indispensable relevance. An increase in overall system efficiency depending on the specific engine system is subjected to a variety of conflicting goals (efficiency, emissions behavior, customer requirements, etc.) and therefore requires efficient research and development tools. Light-induced fluorescence is a tried and tested tool for questions of a qualitative [1] and quantitative [2] nature. This study presents a pragmatic test system for investigating the interactions of laser and LED radiation with fluorescence tracers and liquids as well as two inexpensive high-power light sources which can be used for in-cylinder high-speed observations [3, 4]. The influencing parameters concentration, temperature and aging are examined with engine oils for modern downsizing units with three different oil/tracer combinations in their fluorescence behavior. In addition, an oil/tracer combination is assessed after the use in a combustion engine at a pre-ignition load point. Furthermore, the concentration behavior of a fuel/tracer combination is characterized. With these findings, especially qualitative engine LIF experiments can

✉ Thorsten Schweizer
thorsten.schweizer@kit.edu

Heiko Kubach
heiko.kubach@kit.edu

¹ Institut für Kolbenmaschinen (IFKM), Karlsruher Institut Für Technologie (KIT), Kaiserstraße 12, 76131 Karlsruhe, Germany

be efficiently planned and designed. One application is the tracking of engine operating media movements and accumulations within the combustion chamber via minimally invasive endoscopic accessibilities, which can be used for pre-ignition mechanism synthesis [3, 4]. In the following, the physical principles of fluorescence and fluorescence quenching that are relevant to understand the results shown are briefly outlined. For a more detailed description of the complex molecular processes, reference should be made to the relevant specialist literature [5].

1.1 Principle of light-induced fluorescence

For certain molecules, fluorescence can result from a three-step process (see Fig. 1). In the first step the light energy of a photon (external excitation light source) is absorbed; an excited electron state S_2 occurs (excitation). In the following excited state, which is limited in time, there are conformational changes in the molecule and a large number of possible interactions with its environment. Due to energy dissipation, the fluorescence energy level S_1 is below the excitation energy level. This energy level can be emptied by further processes (static and dynamic quenching, Förster resonance energy transfer or intersystem crossing), which reduces the quantum yield of the fluorescence radiation. In the third step, the molecule returns to its ground state S_0 , releasing photons (emission). The energy difference resulting from the dissipation in the second step is known as the Stokes shift [6].

1.2 Fluorescence quenching

A reduction in the fluorescence intensity can be triggered by a wide variety of processes and is generally called (fluorescence) quenching. The excitation is deactivated without the emission of a photon. Basically, there is dynamic and

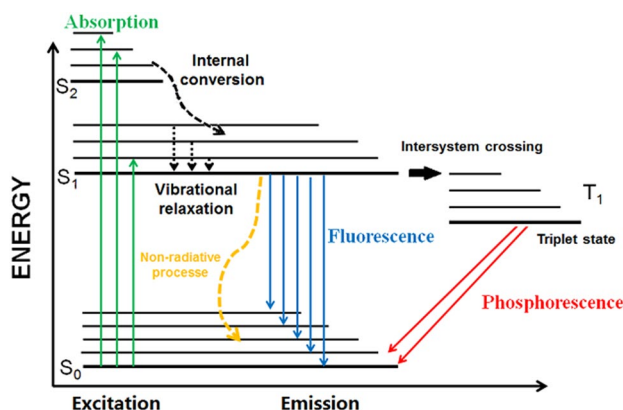


Fig. 1 Perrin Jablonski diagram of fluorescence and phosphorescence (Photophysics of fluorescent proteins 2020 [12])

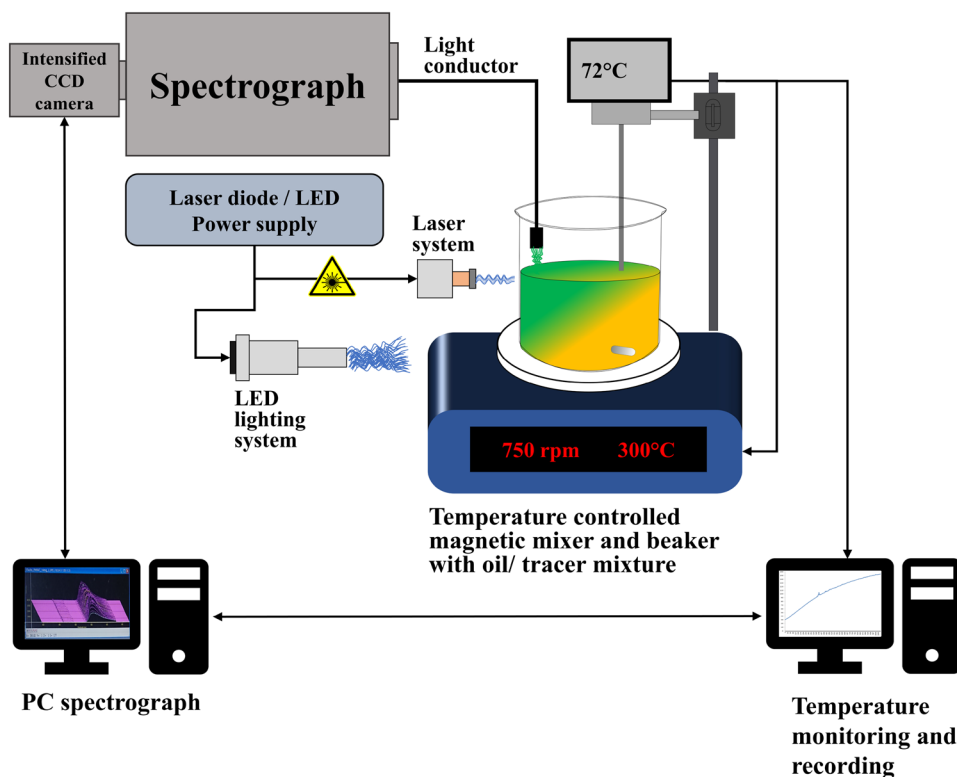
static fluorescence quenching. With dynamic fluorescence quenching, also called collision fluorescence quenching, the excited state of the fluorophore is deactivated by contact with another molecule (quencher) in the solution. There are a large number of molecules that can act as collision quenchers. A very prominent representative is oxygen. Quenching effects can also appear between the fluorescent molecules themselves, which is also known as concentration fluorescence quenching. In addition to the diffusion and collision-dominated effects, the complex formation of fluorescence quenchers and fluorophores in the ground state can lead to a loss of intensity. These processes are known as static quenching. In addition, quenching effects can also occur due to non-molecular processes such as the absorption of excitation light by specific species. Long exposure to excitation light can also lead to photobleaching (chemical quenching). The ability of a molecule to fluoresce can be permanently destroyed [5].

2 Investigation system and methodology

Figure 2 shows an overview of the applied LIF examination system. An Acton SP2556 optical spectrometer from Princeton Instruments (focal length of 500 mm) with a 200 μm entrance slit in combination with the image-intensified CCD camera Princeton Instruments PI-MAX is used to record the emission spectra. The maximum resolution corresponds to 1024×256 pixels. The grating used for all experiments was 150 g/mm, which results in a detection range of approximately 192 nm. The resolution is approx. 0.2 nm. A fiber optic bundle with optical transmission of 190–1100 nm is used as a light guide for receiving and introducing the fluorescent light, which is held at right angles to the excitation light source in the beaker at a small distance above the liquid. The recording is made via the Spectrograph PC using WinSpec software. The trigger signal is recorded by an additional measuring unit for the fluorescence spectrum/temperature correlation.

The excitation light is introduced on the side of the beaker just below the surface of the liquid at a short distance. For this purpose, the LED and laser systems are each fixed in a defined manner with a support structure. The light sources are energized shortly before the start of the measuring point via a laboratory power supply unit with defined parameters for a quantitative comparison of fluorescence intensity within a series of measurement. The excitation light intensity, defined by the set current, was slightly adapted for the specific tracer/fluid combination considering the intensity measuring range (Stoke-shifted fluorescent light) of the spectrometer. A quantitative comparison between the measurement series is only partially meaningful due to specific sources of measurement errors or uncertainties listed

Fig. 2 Scheme of the fluorescence investigation system with signal paths



below. Specific intensities of the excitation light were not measured. Using a magnetic stirrer with integrated temperature control, the liquid/tracer mixture can be tempered and stirred in a defined manner. The movement of the liquid leads to a more homogeneous temperature distribution and avoids the cross-influence of photobleaching effects on the measurement results.

2.1 Engine operating media, light sources and tracer

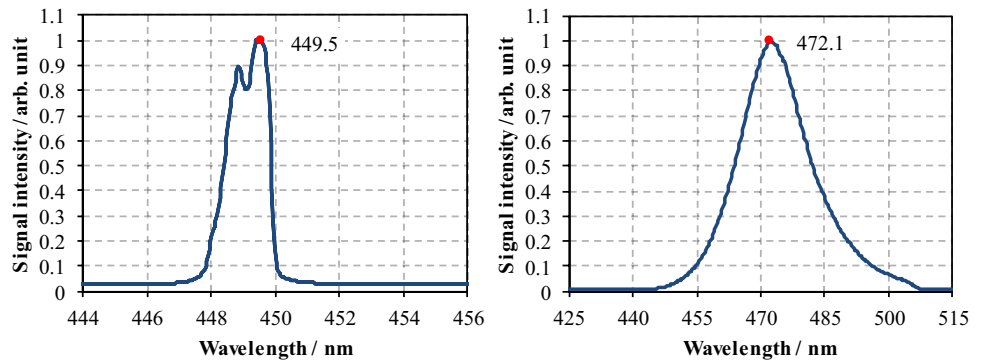
The oil/tracer tests were carried out with the engine oils Fuchs Titan Supersyn F ECO-B 5 W-20 (Fuchs 5W20), Titan Supersyn F Eco-DT 5 W-30 (Fuchs 5W30) and Castrol Magnatec Stop-Start 5 W-20 E (Castrol). These are oils especially designed for modern Ford gasoline and diesel engines. The fuel/tracer tests were carried out with CORYTON advanced fuels “High LSPI” fuel. It has a RON value of 96.5 and is in accordance with the DIN EN 228 standard (DIN EN 228 [7]).

Light sources for engine examinations and especially for the implementation of LIF measurements should have a narrow spectral range and a high beam power. In addition, a compact design is advantageous for an efficient engine system integration. For the presented results a compact 7 W laser diode (NUBM44) with 3 optical lenses for beam shaping as well as a high-performance LED (Osram OSTAR® Projection Power LE B P3W 01) were used. Both light

sources were typically operated with about 2.5 A direct current. The LED was cut in her spectral range with a 500 nm short-pass filter (SPF) and her light is guided to the beaker via a quartz glass rod through an engine access sleeve. The specific emissions spectra from the lighting systems can be seen in Fig. 3.

Three fluorescence tracers have been examined: BASF Oracet® Yellow 084 (452.5 g/mol) (Oracet® 084), Honeywell Lumilux® Yellow CD 345 (555.8 g/mol) (Lumilux® CD 345), Pyrromethene 567A (374.3 g/mol) (PM567A). These could be directly dissolved in the media and showed a clear fluorescence response when excited with the featured light sources. Pyrromethene 597-8C9 also showed good solubility but not a good quantum yield with the light sources. DCM and Rhodamine 6G could not be directly dissolved in the described engine oils. However, it should be pointed out that there are various mediators for the dissolution of these tracers, which were not considered in this study. This was derived from the idea of influencing the properties of the engine operating media as little as possible. Interesting solvents, considering the later use in engine oil, for DCM could be n-Hexane, n-Propanol and Vaseline oil [8]. The absorption of DCM dye in ethanol is described in [9]. The fluorescence characteristics of Rhodamine 6G in ethanol and butanol are investigated in [10]. Detailed different organic solvents effects of Rhodamine 6G can be found in [11].

Fig. 3 Spectra of the light sources used (left: laser diode at 0.5 A; right: LE B P3W 01 with 500 nm SPF)



2.2 Sample preparation

Fresh oil and fuel were each weighed to 200 ml and enriched with the specific tracer quantities in Duran beakers. The tracer quantities were prepared using a precision balance (Sartorius ENTRIS224-1S). For mixing, the fuel/tracer mixtures were each stirred for 5 min using a magnetic stirrer at 1500 rpm. Afterwards the oil/tracer mixtures were also dissolved in an ultrasonic bath at 60 °C for 20 min.

2.3 Investigation methodology

For LIF applications, in addition to the general spectral response due to the combination of light, medium and tracer, knowledge of temperature, concentration and aging behavior is necessary for the design of the experiment.

To investigate the fluorescence characteristics (intensity, spectrum) of different tracer concentrations in oil and fuel, a defined amount of tracer is dissolved in the liquid medium (200 ml) and then spectrally examined at 30 °C in the beaker when excited by laser or LED light. Starting with the smallest amount of tracer, the concentration is consecutively increased in discrete steps in the same beaker. The beaker is removed for preparation after each measurement and then reinserted into the measuring device. Defined stops ensure a constant measuring position for the beaker, light introduction and fluorescence signal recording. The respective concentration series are recorded at constant temperature, spectrometer and light source parameters to ensure a quantitative relative comparison within a measurement series. The spectrometer (amplification factor, exposure time) and light source parameters (voltage, current) are coordinated with each other before each series of examinations so that the lowest expected fluorescence intensity clearly stands out from the measurement noise and the strongest fluorescence intensity does not exceed the maximum measurement limits. A quantitative comparison of different measurement series is therefore not permitted.

To examine the fluorescence characteristics (intensity, spectrum) of specific tracer concentrations at different oil

temperatures, an oil/tracer combination in the beaker is continuously heated up to 150 °C on a magnetic stirrer. The heating behavior is determined by the settings of the internal control circuit of the magnetic stirrer (PID controller) and recorded via an external unit. The same setting parameters (plate temperature: 300 °C, target temperature 170 °C) are used for all temperature tests presented. From 30 °C, three spectrographic measurements are carried out every 10 °C. A stir bar (750 rpm) in the asymmetrically attached beaker ensures a more homogeneous temperature distribution in the oil volume. Spectrometer and light source parameters are set as described above.

To characterize the aging behavior, two specific oil/tracer mixtures were subjected to two temperature series measurements with an interval of one week each (stored in the beaker at room temperature). In the second attempt, the samples are thus subject to a temperature and time history. In addition, an oil/tracer combination was used as lubricating oil in a combustion engine and spectrally examined after the use in a twenty-minute pre-ignition operation (1600 rpm, 200 Nm, BMEP 25.2 bar). This resulted in great mechanical stress and contamination with fuel and combustion residues of the oil/tracer combination.

Reference should be made to the following specific sources of measurement errors or uncertainties in the examination system:

The mixing process of medium and tracer can lead to concentration fluctuations. A slight rotational position change of the beaker can lead to an influence of different wall thicknesses on the light intensity and refraction. The media expansion during a temperature series results in a change in the distance between the position of the liquid surface and the light guide.

3 Results and discussion

For each measurement, all spectral measurement results consist of the mean value of three individual measurements taken in quick succession. The examined tracer/liquid

combinations represent a very complex system due to the large number of different molecules and the associated great potential for interaction. The mechanisms mentioned in the discussion are only intended to represent a rough classification of the general topic and not claim to be complete.

3.1 Self-fluorescence engine operating media

Figure 4 shows the self-fluorescence spectrum of the engine oils Fuchs 5W20 and Castrol (left) when excited with the laser diode, normalized to the maximum intensity as well as laser light passing through the “High LSPI” fuel without generating a fluorescence answer (right). Due to the very weak fluorescence signal and the necessary amplification factors on the spectrograph, the laser excitation source can be clearly seen (at ~ 465 nm) and exceeds the signal strength of the autofluorescence despite right-angled signal recording. The spectrum of the laser diode is slightly red-shifted due to the high operating temperature. The measuring range of the spectrograph ends shortly after 625 nm. The maxima of the emission spectra are around 520 nm for Fuchs 5W20 and 530 nm for Castrol. When the “High LSPI” fuel is irradiated, no self-fluorescence can be detected for any light source.

Fig. 4 Self-fluorescence spectra of Castrol (purple, dashed) and Fuchs 5W20 (green) (left); Laser beam passing through “High LSPI” fuel (right)

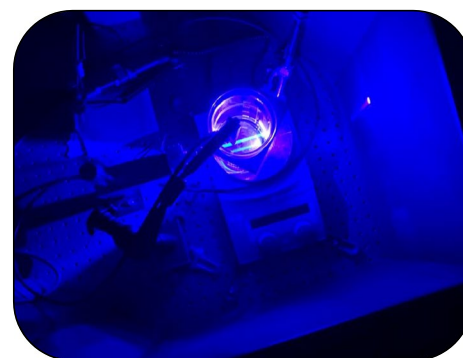
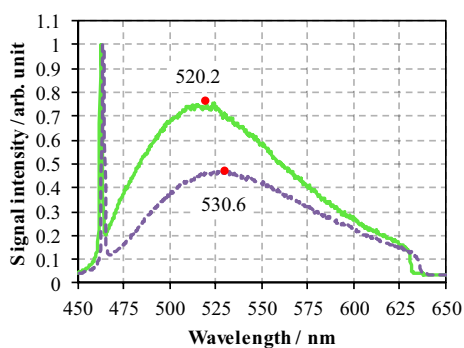
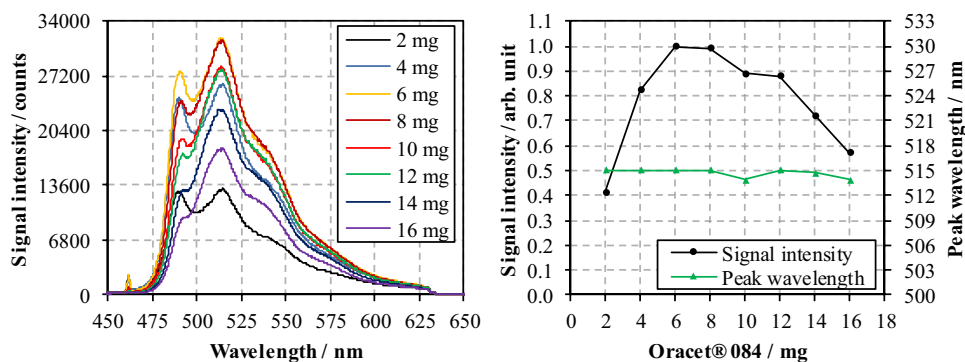


Fig. 5 Emission spectra of Oracet[®] 084 in 200 ml Fuchs 5W20 (30 °C) with different tracer concentrations (left); Normalized signal intensity and peak wavelength as a function of the Oracet[®] 084 concentration in 200 ml Fuchs 5W20 (right)



3.2 BASF Oracet[®] yellow 084

3.2.1 Concentration characterization

Figure 5 shows the emission spectra of Oracet[®] 084 at 30 °C in Fuchs 5W20 at different tracer concentrations and the associated standardized signal intensity and peak wavelength as a function of the concentration when excited by means of a laser diode. The temperature-shifted excitation spectrum of the laser diode can be seen in the area around 465 nm.

(In comparison to Fig. 3, the spectrum shift results in particular from the operation of the diode with larger numbers of amperes.) The spectrum is characterized by a double peak at 490 and 515 nm and is strongly dependent on the concentration. With increasing tracer concentration, the relative signal intensity difference between the peaks increases and the 515 nm peak becomes increasingly dominant. A self-fluorescence excitation that increases with the concentration can be responsible for this. No relevant peak wavelength change can be observed. The concentration-dependent maximum fluorescence intensity shows a maximum in the range between 6 and 8 mg Oracet[®] 084. Thereafter, probably the increase in dynamic quenching effects in the form of increasing collision quenching leads to a decreasing fluorescence intensity. At 16 mg the solubility limit seems to be reached, which is characterized by the tracer molecules beginning to settle on the bottom of the beaker.

Oracet® 084 also shows comparable double peak characteristics in Castrol oil (Fig. 6). The emission maximum for the investigated step size of 3 mg is at 6 mg Oracet® 084. A change in peak wavelength is not observed. The relative signal intensity difference between the peaks increases and, at high concentrations, leads to a strong decrease in the first peak. The underlying physical effects could be analogous to the 5W20 sample.

3.2.2 Temperature and aging characterization

To characterize the temperature dependence of the emission spectrum on specific tracer concentrations, this is recorded in 10 °C steps from 30 to 150 °C oil temperature. Aging is shown by running a temperature series twice per concentration at a time interval of one week.

Figure 7 shows the emission spectra of 7 mg Oracet® 084 in 200 ml Fuchs 5W20 at different mixture temperatures during the second heating cycle and the associated standardized signal intensity and peak wavelength as a function of the temperature when excited by means of a laser diode. 7 mg was in the concentration area of maximum signal intensity at 30 °C in the concentration characterization test. As a result of the increase in oil temperature, there are more and more quenching effects and thus a pronounced decrease in fluorescence intensity down to about 40% of the initial level. The

increase in the temperature-dependent diffusion potential presumably leads to severe collision quenching. The first emission peak decreases over proportionally with increasing temperature and the spectrum becomes single peaked. The Stokes shift remains constant.

Figure 8 shows the normalized signal intensities and peak wavelengths as a function of temperature, concentration and number of tempering when excited by means of a laser diode in Fuchs 5W20. The two concentrations 7 mg and 16 mg show a marked difference in temperature behavior. When the 7 mg mixture is heated for the first time, the fluorescence intensity increases to 70 °C and then drops to about 60% of the maximum intensity at 150 °C. The spectrum at 30 °C and 150 °C shows a slightly enlarged Stokes shift. There is a comparable peak behavior to Fig. 7. In general, additional oxidation effects of the oil seem to influence the system behavior. The second heating, however, leads to a continuous decrease in intensity to about 40% of the initial level and shows a constant Stokes shift. The first heating of the 16 mg mixture leads to a continuous decrease to below 20% of the maximum intensity with a slight increase (approx. 2%) in the last temperature point. The Stokes shift remains at a constant level with a slight increase at 150 °C. Compared to the 7 mg mixture, it is on a slightly higher level. The second heating of the 16 mg mixture leads to a continuous decrease in the fluorescence

Fig. 6 Emission spectra of Oracet® 084 in 200 ml Castrol (30 °C) with different tracer concentrations (left); Normalized signal intensity and peak wavelength as a function of the Oracet® 084 concentration in 200 ml Castrol (right)

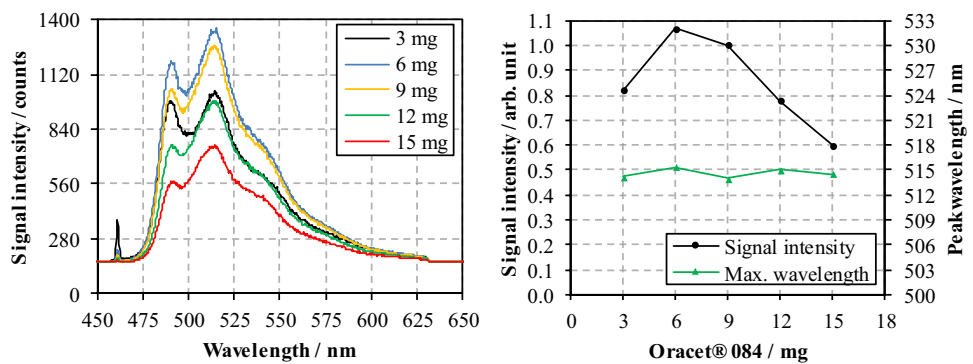


Fig. 7 Emission spectra of Oracet® 084 (7 mg) in Fuchs 5W20 (200 ml) at different temperatures during the second heating (left); Normalized signal intensity and peak wavelength as a function of temperature (right)

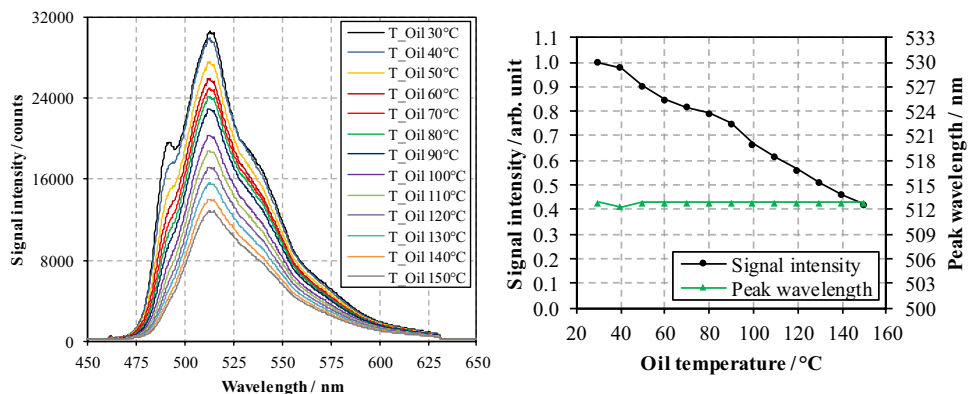


Fig. 8 Normalized signal intensity (left) and peak wavelength (right) as a function of the temperature of different Oracet® 084 concentrations and the number of temperature series in 200 ml Fuchs 5W20

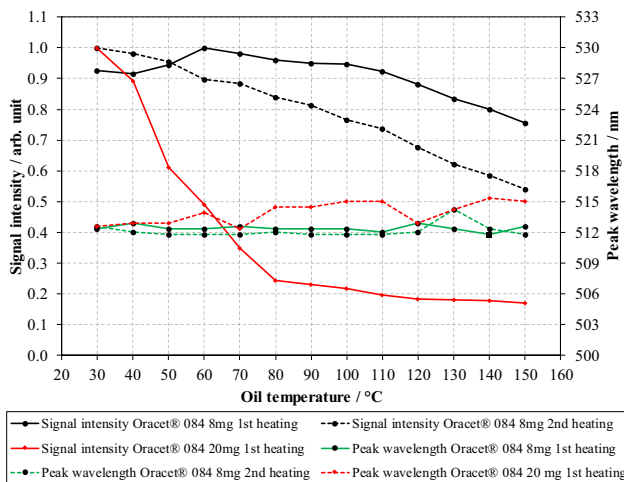
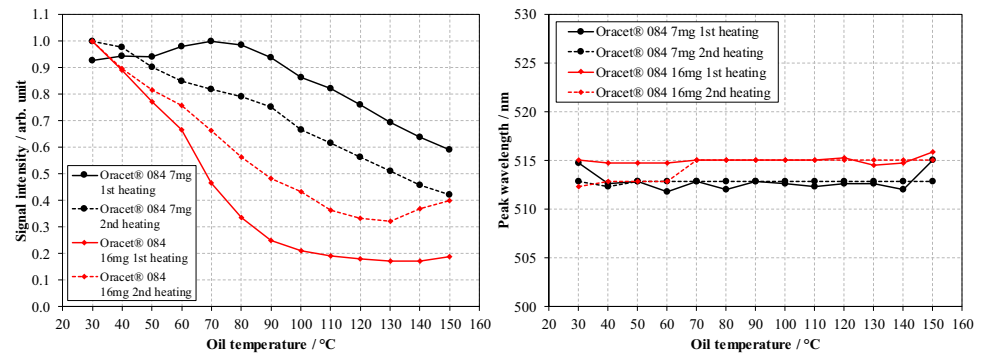


Fig. 9 Normalized signal intensity and peak wavelength as a function of the temperature of different Oracet® 084 concentrations and the number of tempering in 200 ml Castrol

intensity up to 130 °C to about 32% of the initial intensity, after which a slight increase to about 40% at 150 °C can be observed. The Stokes shift in the temperature range of 30–60 °C is at the level of the 7 mg mixture. From 70 °C it corresponds to the level when the 16 mg mixture was heated for the first time.

Figure 9 shows the normalized signal intensities and peak wavelengths as a function of temperature, concentration and number of tempering when excited by means of a laser diode in 200 ml of Castrol. In Castrol oil there is a very comparable picture. When heated for the first time, the 8 mg mixture shows its maximum intensity at 60 °C, after which it drops to about 75% of the maximum intensity. The second heating leads to a continuous decrease in intensity to about 54% of the initial intensity. Both series of tests show an approximately constant Stokes shift. The significantly higher dosed sample (20 mg) shows a very strong drop to 80 °C to about 24% of the initial intensity when heated for the first time. At 150 °C it still has about 17% of the intensity. In the Stokes shift, an increased level can be observed, especially from

80 °C. (A second heating with the Castrol oil was not carried out.)

Higher concentrations show a greater variance in the gradient of the signal intensity curve. An initial steeper decrease and a flatter course at higher temperatures, which generally speaks for increased interactions compared to low tracer dosages. It can be assumed that a slightly increased concentration in comparison to the 30 °C maximum intensity concentration could be advantageous for temperature and aging effects with regard to a maximum fluorescence intensity. Higher concentrations tend to shift the emission spectrum slightly to red, especially under the influence of temperature.

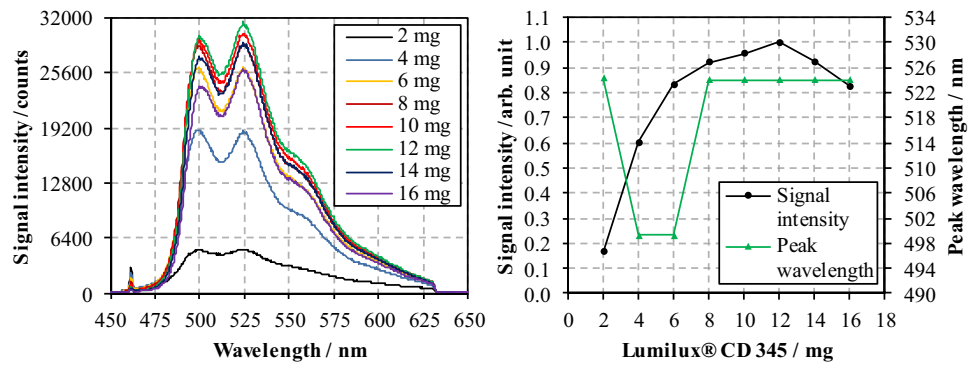
3.3 Honeywell Lumilux® yellow CD 345

3.3.1 Concentration characterization

Figure 10 shows the emission spectra of Honeywell Lumilux® CD 345 in Fuchs 5W20 (30 °C) at different tracer concentrations as well as the associated standardized signal intensity and peak wavelength as a function of the concentration when excited by means of a laser diode. In the area around 462 nm, the temperature-shifted excitation spectrum of the laser diode can be seen again. The spectrum is characterized by a double peak (499 and 524 nm) and is strongly dependent on the concentration. A signal intensity difference between the peaks that increases relative to the concentration can only be observed weakly. The second peak becomes more dominant as the concentration increases. The concentrations 4 and 6 mg show a slightly dominant first peak, which is why there is a peak wavelength shift here. The concentration-dependent fluorescence intensity shows a maximum in the range around 12 mg Lumilux® CD 345. After that, quenching effects will probably occur more intensely, analogous to Oracet® 084.

Figure 11 shows the emission spectra of Lumilux® CD 345 in Coryton “High LSPI” fuel (17 °C) at different tracer concentrations as well as the associated standardized signal intensity and peak wavelength as a function of the concentration when excited by LED light. In contrast

Fig. 10 Emission spectra of Lumilux® CD 345 in Fuchs 5W20 (30 °C) with different tracer concentrations (left); Normalized signal intensity and peak wavelength as a function of the Lumilux® CD 345 concentration in Fuchs 5W20 (right)



to the oil, the spectrum is characterized by a single peak at 527 nm and is strongly dependent on the concentration. The single peak characteristic must be due to the different molecular composition of the liquid. The concentration-dependent fluorescence intensity shows a maximum in the range between 26 and 33 mg Lumilux® CD 345. After that, the quenching effects increase again. In a direct comparison to engine oil, there is a significantly better solubility and a greater concentration potential.

3.3.2 Temperature and aging characterization

The characterizations take place analogously to the Oracet® 084 examinations. Figure 12 shows the emission spectra of 11 mg Lumilux® CD 345 in 200 ml Fuchs 5W20 at different mixture temperatures during the second heating cycle and the associated standardized signal intensity and peak wavelength as a function of the temperature when excited by means of a laser diode. As a result of increasing quenching effects, there is a pronounced decrease in fluorescence intensity down to 37% of the initial level with increasing oil temperature. In all temperature series, the first emission peak

Fig. 11 Emission spectra of Lumilux® CD 345 in Coryton “High LSPI” (17 °C) with different tracer concentrations (left); Normalized signal intensity and peak wavelength as a function of the Lumilux® CD 345 concentration in Coryton “High LSPI” (right)

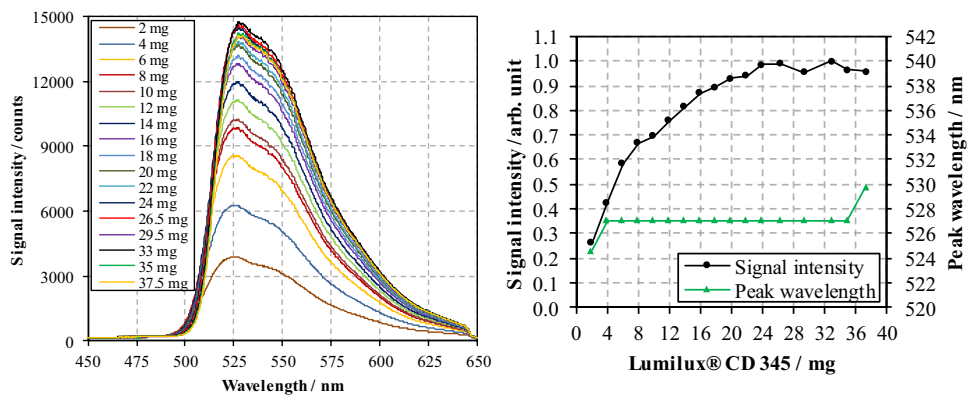
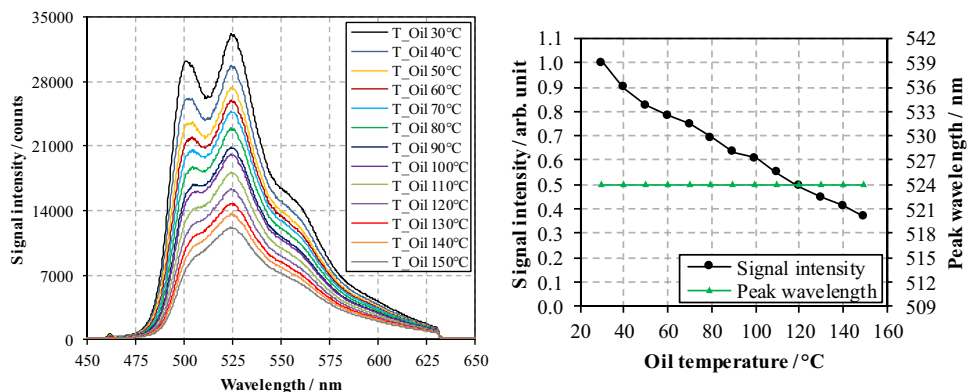


Fig. 12 Emission spectra of Lumilux® CD 345 (11 mg) in Fuchs 5W20 (200 ml) at different temperatures during the second heating (left); Normalized signal intensity and peak wavelength as a function of temperature (right)



decreases with increasing temperature and the spectrum becomes single peaked. The Stokes shift remains constant.

Figure 13 shows the normalized signal intensities and peak wavelengths as a function of temperature, concentration and number of tempering when excited by means of a laser diode (Fuchs 5W20). The two concentrations 11 mg and 16 mg show a marked difference in temperature behavior. When the 11 mg mixture is heated for the first time, there is a sharp drop in intensity up to 60 °C and a subsequent increase to 80 °C until it drops again to around 46%. The second heating, however, leads to a continuous decrease in intensity to about 37% of the initial level. Both temperature series show a constant Stokes shift. Here, too, oil oxidation effects seem to influence the fluorescence. The first heating of the 16 mg mixture leads to a continuous decrease in the fluorescence intensity with the exception of the 90 °C value to a final level of approx. 31%. The Stokes shift remains at a constant level with slight fluctuations. The second heating leads to a continuous decrease to 46% of the maximum intensity. The Stokes shift is constant with the exception of the 30 °C value. In general, the second temperature series

shows a more comparable temperature behavior of the different concentrations. Higher concentrations show again a greater variance in the gradient of the signal intensity curve. Overall, Lumilux® CD 345 and Oracet® 084 show a very comparable system behavior. Again, a slightly increased concentration in comparison to the 30 °C maximum intensity concentration could be advantageous for temperature and aging effects with regard to a maximum fluorescence intensity. Aging investigations of fuel/tracer mixture have not been done due to the fuel evaporation characteristics.

3.4 Pyromethene 567A

3.4.1 Concentration characterization

Figure 14 shows the emission spectra of PM567A in Fuchs 5W20 (30 °C) at different tracer concentrations and the associated standardized signal intensity and peak wavelength as a function of the concentration when excited by means of a laser diode. The spectrum has a peak at 546 nm and is strongly dependent on the concentration. A slight redshift

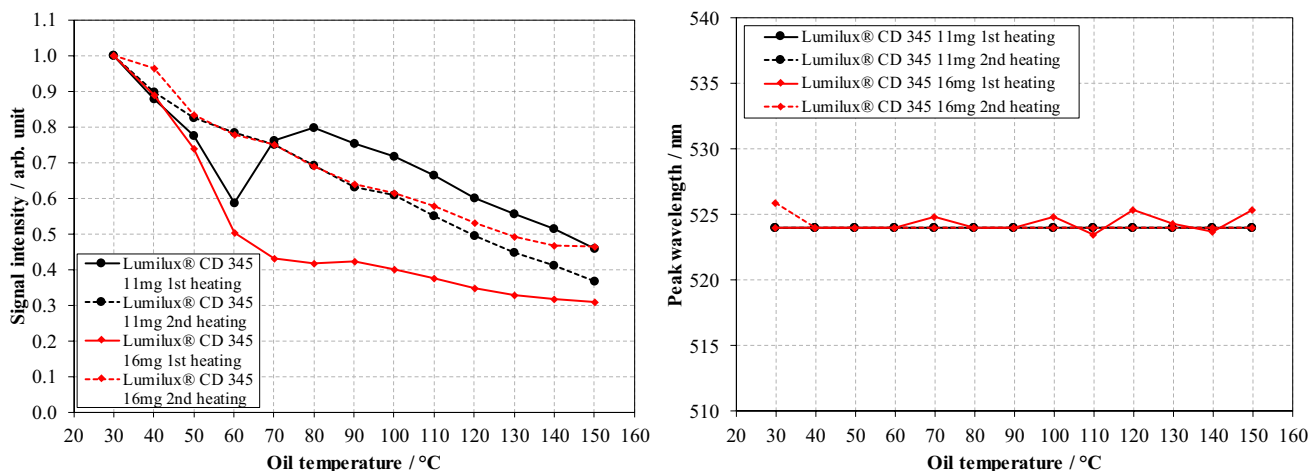
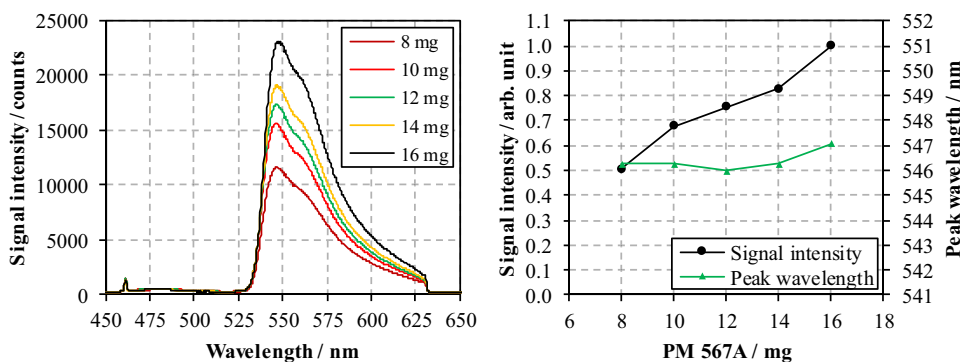


Fig. 13 Normalized signal intensity (left) and peak wavelength (right) as a function of the temperature of different Lumilux® CD 345 concentrations and the number of temperature series in 200 ml Fuchs 5W20

Fig. 14 Emission spectra of PM567A in Fuchs 5W20 (30 °C) with different tracer concentrations (left); Normalized signal intensity and peak wavelength as a function of the PM567A concentration in Fuchs Titan Super 5W20 (right)



with increasing concentration can be seen. Up to 16 mg a steady increase in intensity is visible and a slight redshift is indicated. The concentration limit is not reached.

Figure 15 shows the emission spectra of PM567A in Fuchs 5W30 (30 °C) at different tracer concentrations and the associated standardized signal intensity and peak wavelength as a function of the concentration when excited by means of LED light. The excitation spectrum of the LED can be observed weakly in the range around 468 nm. The spectrum shows an increasing redshift with increasing concentration. Up to 25 mg PM567A, a flat increase in intensity is visible, which indicates that the maximum concentration potential will soon be reached.

3.4.2 Temperature and aging characterization

Figure 16 shows the emission spectra of 16 mg PM567A in 200 ml Fuchs 5W20 at different mixture temperatures in the second heating cycle and the associated standardized signal intensity and peak wavelength as a function of the temperature when excited by means of a laser diode. With the exception of the 70 °C value, a constant drop in intensity down to approx. 19% can be observed. In contrast to Oracet® 084 and Lumilux® CD 345, PM567A shows a pronounced redshift with increasing temperature.

Figure 17 shows the normalized signal intensities and peak wavelengths as a function of temperature, concentration and number of tempering when excited by means of a laser diode in Fuchs 5W20 and in Fuchs 5W30. Both temperature series with 16 mg and excitation by means of a laser diode show a very similar behavior in terms of both the decrease in intensity and the redshift. The concentration of 25 mg in Fuchs 5W30 also shows a comparable intensity behavior, but with a flatter intensity loss curve up to 70 °C. An overall larger Stokes shift can be observed due to the higher concentration. Despite the greatest loss of intensity, PM567A shows the most similar behavior across all test series, which suggests good temperature stability. (A second heating with 25 mg PM567A was not carried out.)

3.5 Spectral comparison

Figure 18 shows the spectral comparison of the tracers examined in Fuchs 5W20 when excited with a laser diode and LED. The laser spectra are recorded at an oil temperature of 120 °C, whereas the LED spectra are recorded at 30 °C. This can be seen in the temperature-sensitive Stokes shift of PM567A. Otherwise the characteristic features of the emission spectra are very similar. The tracer amounts have been 7 mg for Oracet® 084, 11 mg for Lumilux® CD 345 and 16 mg for PM567A. Oracet® 084 has the smallest

Fig. 15 Emission spectra of PM567A in Fuchs 5W30 (30 °C) with different tracer concentrations (left); Normalized signal intensity and peak wavelength as a function of the PM567A concentration in Fuchs 5W30 (right)

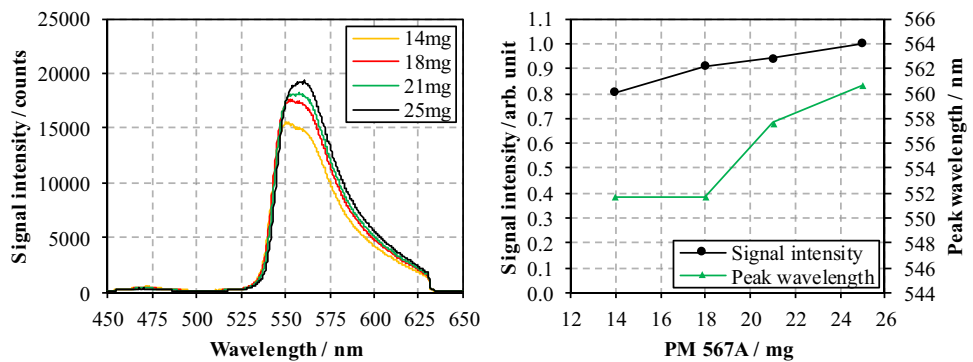
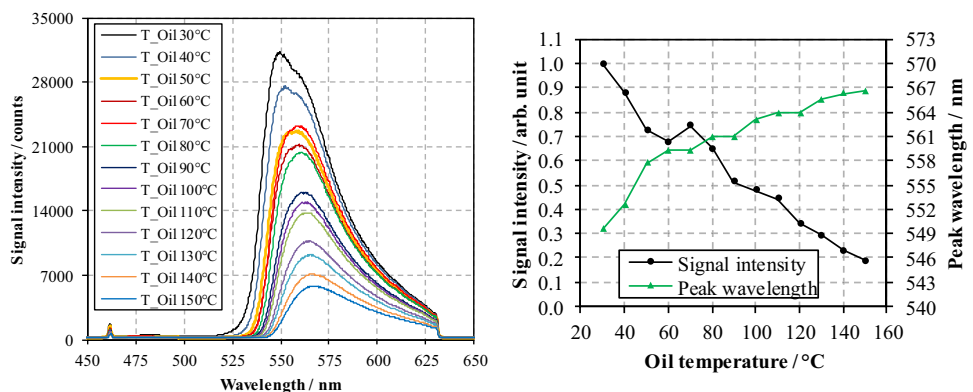


Fig. 16 Emission spectra of PM567A (16 mg) in Fuchs 5W20 (200 ml) at different temperatures during the second heating (left); Normalized signal intensity and peak wavelength as a function of temperature (right)



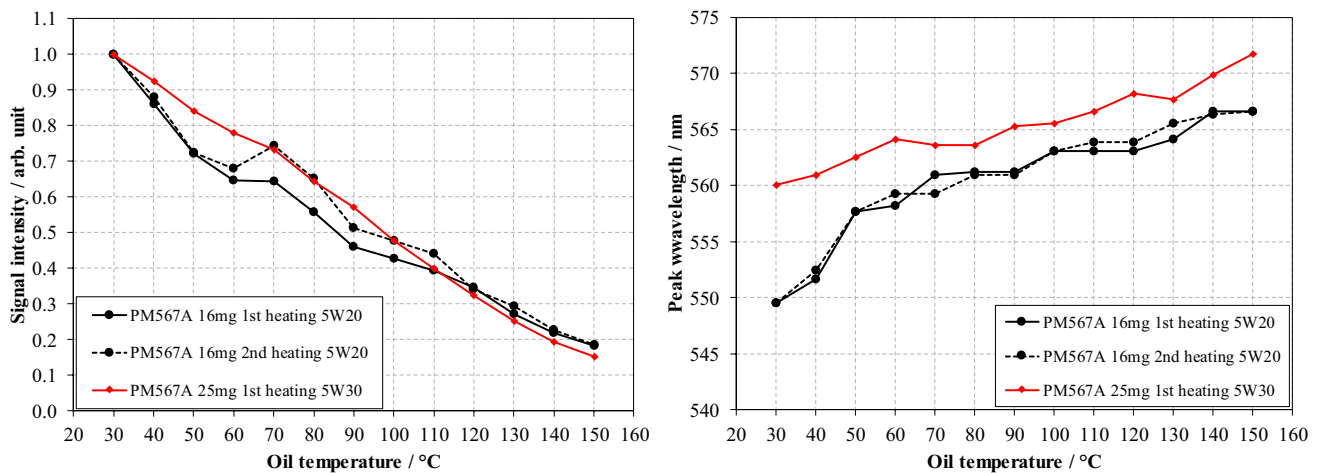


Fig. 17 Normalized signal intensity (left) and peak wavelength (right) as a function of the temperature of different PM567A concentrations and number of tempering

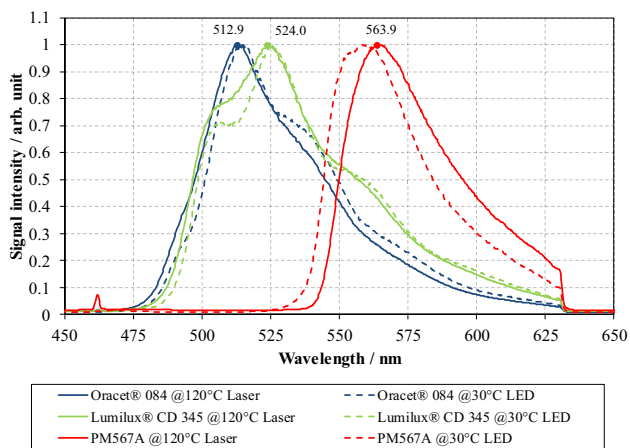


Fig. 18 Spectral overview of the examined tracers at 30 °C (LED) and 120 °C (Laser) in 200 ml Fuchs 5W20

Stokes shift with 58 nm, followed by Lumilux® CD 345 with 62 nm. PM567A has the largest Stokes shift with 102 nm. The 120 °C oil temperature comparison was chosen because of real word engine oil temperatures. In general, both lighting sources give a similar fluorescence picture.

3.6 Use in engine operation

In engine tests with a modern downsizing unit, a fresh engine oil batch of 3.75 L Fuchs 5W30 was mixed with 300 mg PM567A ($\hat{=}$ 16 mg/200 ml) and a 20 k cycle pre-ignition test was carried out. This 25 min full load engine operation puts great mechanical, thermal and chemical stress

on the tracer/oil mixture. Subsequently, a drained 200 ml oil sample was spectrally examined when excited by means of LED light. The results are shown in Fig. 19. For comparison, the spectrum of a fresh 16 mg/200 ml PM567A/Fuchs 5W30 sample at 30 °C when excited by means of LED is shown.

Despite the harsh conditions in the engine, the tracer remains active and shows the expected behavior. In a direct comparison, the maximum of the emission spectrum is spectrally blue-shifted, which is probably due to the concentration reduction by fuel dilution. The comparable intensity of the excitation light and emission spectrum in the engine-driven oil/tracer sample in the diagram is striking, which indicates a very low general fluorescence intensity. This statement can be made on the basis of the experimental design: excitation light introduction is placed in a right angle to the fluorescence light recording. Hence the intensity difference between excitation light and fluorescence light increases drastically. This is, among other things, due to the changed optical oil properties, in particular due to combustion residues and fuel dilution, as well as the specific structure of the examination system. Figure 20 shows an application-related investigation example on an engine with minimally invasive endoscopic accessibilities. The fluorescence signal is observed by on long-pass filtered camera via an endoscope. The excitation light is introduced into the combustion chamber via two short-pass filtered LED engine lighting systems (adaption of spectral range). Due to the spectral range of the LED's the use of a 525 nm long-pass filter for a clear separation of excitation light and fluorescence light is necessary. Hereby a large stoke shift relates to better fluorescence light detection efficiency. Specific fuel accumulations can be detected at the liner bore top area after

Fig. 19 Spectral comparison between an oil/tracer mixture used in an internal combustion engine and a fresh oil/tracer mixture

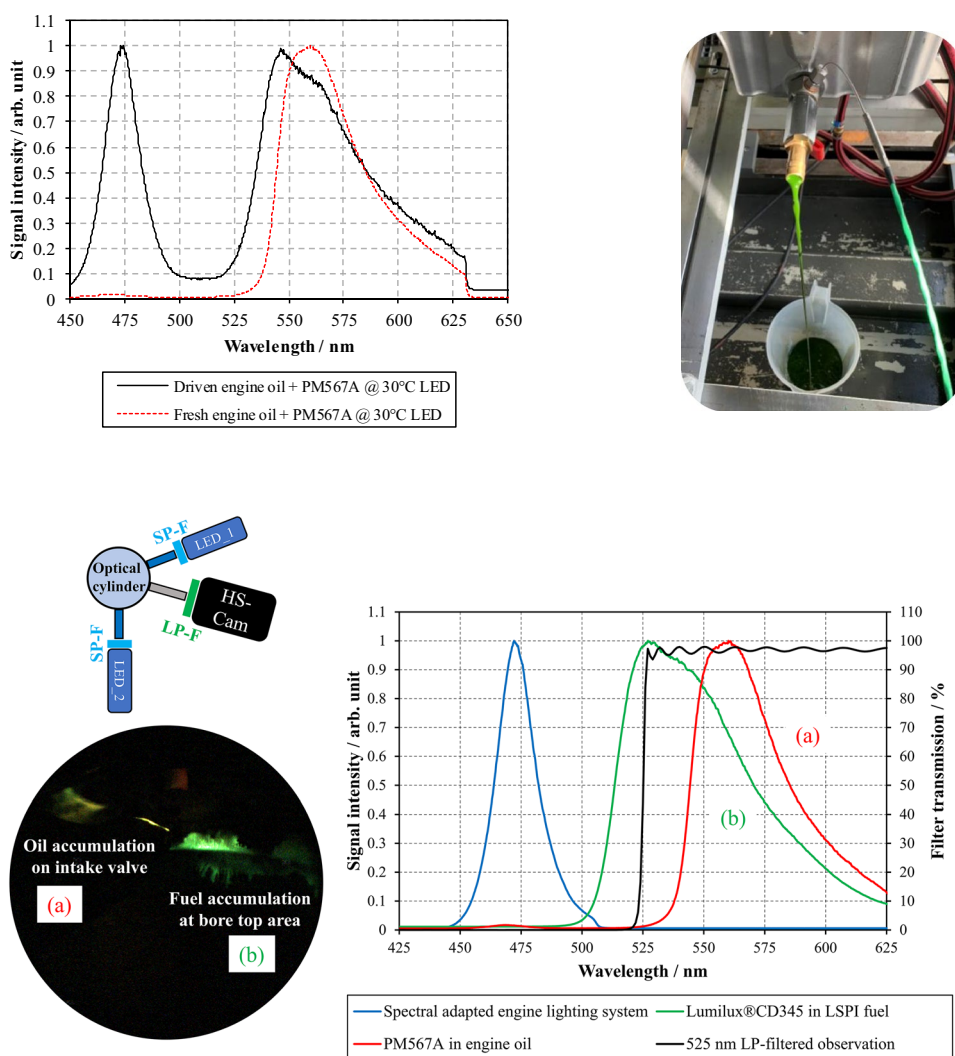


Fig. 20 Exemplary use of doped engine operating media for in-cylinder accumulation investigations with an engine LIF setup

full load engine operation, which further correlate to local deposit build-up; a sub-mechanism to pre-ignition initiation. In this special case oil accumulations on the intake valve after pre-ignition related oil injection tests can additionally be detected.

4 Summary and conclusion

In the investigations presented, the fluorescence behavior of Oracet[®] 084, Lumilux[®] CD 345 and PM567A in engine oils when excited by a laser diode or LED was shown. In addition, Lumilux[®] CD 345 was also examined in fuel. The effects of concentration, temperature and aging on the fluorescence spectrum were shown using a pragmatic fluorescence investigations system. Overall, Oracet[®] 084 and Lumilux[®] CD 345 showed very similar behavior, whereas

PM567A sometimes showed significant behavior differences. All tracers though can be used in engine oil.

Oracet[®] 084 has an emission intensity maximum in the tested engine oils at 30 °C in the concentration range of 6–8 mg/200 ml. Lumilux[®] CD 345 shows this at around 12 mg/200 ml for engine oil and around 24 mg/200 ml for “High LSPI” fuel. Both tracers show a very low concentration influence on the Stokes shift. For PM567A, the concentration-dependent fluorescence maximum was not yet reached at 25 mg/200 ml in engine oil. However, the curve trend shows that the maximum concentration potential will soon be reached. There is also a concentration-dependent redshift of the spectrum.

The temperature and aging characteristics are very constant with PM567A. At oil temperatures of 150 °C, a decrease in the fluorescence intensity to below 20% of the initial intensity can be observed. There is also a clear Stokes

shift increase with increasing temperature. Oracet[®] 084 and Lumilux[®] CD 345 show a concentration-dependent temperature and aging behavior with an almost constant Stokes shift. Losses of intensity between 40 and 80% can be observed. With both tracers a slightly increased concentration in comparison to the 30 °C maximum intensity concentration could be advantageous for temperature and aging effects with regard to a maximum fluorescence intensity.

A large Stokes shift is advantageous for qualitative engine observations with the lighting systems used, which is why the PM567A is particularly suitable here.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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