# Two-Color Laser-Induced Fluorescence Thermometry in Micrometric Ethanol Droplets Using a Fluorescein and Sulforhodamine 101 Dye Mixture

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ABSTRACT

In this work, two-color laser-induced fluorescence (2c-LIF) is applied to measure the temperature in micrometric ethanol droplets, containing a novel dye mixture of fluorescein (FL) and sulforhodamine 101 (SRh). A monodisperse droplet generator is used to generate 100 µm sized droplets with temperatures from 293 K to 343 K. The addition and excitation of the dye mixture allow the simultaneous detection of the fluorescence signal with two detection systems. A fiber coupled spectrometer and an imaging system with two sCMOS cameras provide both, spectral and spatial information. Measuring both signals at the same time, lasing effects (or morphology-dependent resonances) in the droplet can be clearly recognized in the spectra and circumvented in further measurements.
Additionally, absorption measurements are conducted, which demonstrate the difference in temperature sensitivity between the two dyes and show potential re-absorption effects. At high temperatures, the photon absorption of FL increases strongly while SRh shows a steady absorption at all temperatures. By measuring the emission spectra, the implied temperature dependence can be observed for FL. On the contrary, the emission signal of SRh is constant at any temperature measured. The wavelength regions with highest sensitivity are elaborated and respective filters are chosen for the color channels in the imaging system. No lasing effects were observed in these filter regions in planar and spectral measurements. Temperature-dependent signal ratios of the two channels are obtained for the detected spectra and images. The resulting calibration curves are compared and discussed. A much steeper slope and thus larger sensitivity is achieved by measuring with the spectrometer. Both calibration curves show only very little standard deviations, which proves the applicability and reliability of the setup, the method and the utilized dyes, for application in technical spray systems.

## 1. Introduction

Atomization processes have a great significance in technical applications, which vary from fuel injection and combustion processes in turbines to other systems in energy and process technology like e.g. cooling, cutting and painting. Therefore, various experimental techniques aim a further analysis of the liquid breakups and evaporation phenomena in sprays. One important quantity influencing the liquid-gas transition is the droplet temperature. In this work, laser-induced

fluorescence (LIF) using a dye mixture dissolved in ethanol is applied for temperature measurements in a monodisperse droplet chain.

Two-color laser-induced fluorescence (2c-LIF) is a promising method to determine the temperature field in gaseous environments and has been successfully applied in several works (Schulz et al., 2005). The temperature is determined by a signal ratio of two detected color channels represented by respective optical filters, transmitting light in wavelength ranges of different temperature dependence. Transferring this approach to the liquid phase opens many challenges like scattering effects at the phase boundaries and the necessity of a suited fluorescence tracer. Various fluorescent dyes, soluble in the respective fluid, have been tested for this approach (Mishra et al., 2016; Prenting et al., 2020). Previous works have reported a successful detection of temperatures in droplets, using photo multiplier tubes (PMT) (Lavieille et al., 2001; Perrin et al., 2015). Using a dye mixture and an imaging system for detection, Chaze et al. performed further temperature measurements in large (mm scale) water droplets, impinging on a surface (Chaze et al., 2017). Prenting et al. conducted temperature field measurements using a single dye (coumarin 153) for consecutive recordings of the two color channels in a SpraySyn burner (Prenting et al., 2020).

Detecting LIF signals from spherical droplets, one demand is the suppression of emerging resonance effects. Due to the shape and the resulting laser light propagation inside the droplet, the phase boundary leads to multiple total reflections. Thus, specific wavelengths are amplified, leading to a pronounced interference signal in the emission spectra. Palmer et al. achieved a suppression of these morphology dependent resonances (MDR) in the spectrum of pyrromethene 597-8C9 using an additional non-fluorescing dye (Oil Blue N) for an enhanced energy transfer (EET) by absorption in the region of the superimposed light (Palmer et al., 2016). A dye mixture is dissolved in ethanol in this work similar to Chaze et al. (Chaze et al., 2017) who proposed fluorescein (FL) and sulforhodamine (SRh) 640.

In the present work we utilized SRh101 (abbreviated as SRh for simplicity) instead of SRh640. The dye selection was modified with regard to solubility and fluorescence signal intensity in ethanol instead of water. With the spectral information, the MDR wavelength region in the dye added droplets in this work could be determined. No suitable additional dye could be found for the purpose of an EET without significant influence on the important emission regions. Instead, the addition of the second fluorescing dye leads to a shift of the MDR to higher wavelength regions compared to the emission spectra of the single dyes, see Fig. 1.

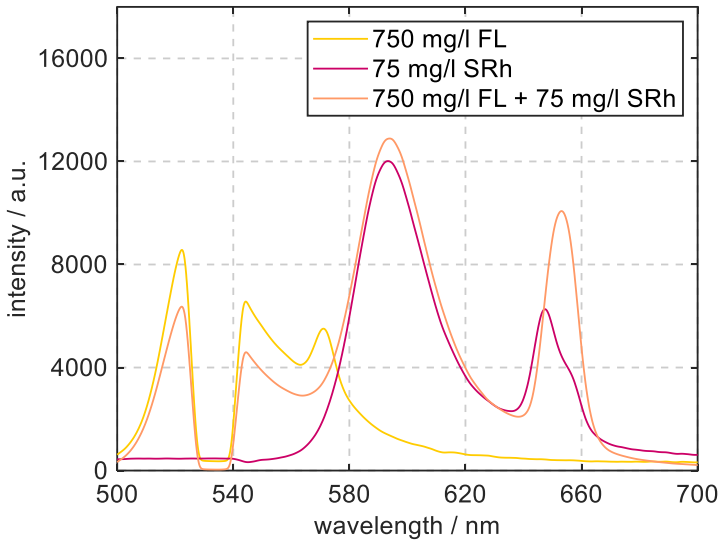


**Fig. 1** Fluorescence emission spectra of ethanol droplets with addition of the dyes FL, SRh and a dye mixture of both FL and SRh. The missing signal around 532 nm is due to the notch filter.

The signal drop around 532 nm is due to the notch filter. At 570 nm the fluorescein spectrum shows the MDR peak. By admixing the second dye, SRh, a redshift of the MDR peak to a wavelength region around 650 nm can be observed. This region is outside of the relevant filter regions (shaded bands in Fig. 4, right), thus MDR signals do not interfere with the spectral regions of the 2c-LIF measurements. Due to re-absorption effects, the "FL peak" (parted by the notch filter) is lowered by the addition of SRh.

## 3. Measurement Setup and Methods

Fig. 2 shows the experimental setup with a pulsed Nd:YAG-laser at 532 nm. The expanded, collimated beam is led through a monodisperse droplet chain, which is adjusted to a droplet size of 100 µm. The droplet generator (FMAG 1520) is connected to recirculating chillers, regulating the ethanol to temperatures from 293 K up to 343 K. The upper temperature is limited by the boiling point of ethanol. Ethanol is dosed with 750 mg/l FL (CAS: 518-47-8) and 75 mg/l SRh (CAS: 60311-02-6). These concentrations are higher than in previous works (Chaze et al., 2016; Mishra et al., 2016), because of the low signal in the micrometric drops. According to Guénot et al. no influence of the dye admixture on the liquid properties could be obtained (Guénot et al., 2020). For verification, measurements of density, surface tension and dynamic viscosity were carried out for three different probes at 293 K, see Tab. 1. Regarding density and surface tension, no changes

could be observed. The dynamic viscosity shows a slight increase with the addition of the highly concentrated FL.

**Tab. 1** Fluid properties of pure ethanol and ethanol with the admixture of the dyes.

| | density / kg/m$^3$ | surface tension / mN/m | dyn. viscosity / mPas |
|---|---|---|---|
| ethanol | 790 | 22.3 | 1.156 |
| ethanol + FL | 790 | 22.3 | 1.194 |
| ethanol + FL + SRh | 790 | 22.3 | 1.194 |

At 90° detection angle a long-distance microscope (Infinity K2 DistaMax) is mounted to an imaging system, including two sCMOS cameras (Imager, LaVision). This system includes a dichroic mirror to split the signal into two wavelength ranges. Both parts of the signal pass through a specific band-pass filter (554/23 BrightLine HC and 615/24 BrightLine HC), only allowing a detection of the shaded color bands as indicated in Fig. 4. On the opposite side of the droplet generator, a spectrometer (USB 4000, Ocean Optics) for spectral detection is fiber-coupled to an optical system consisting of two achromatic doublets and a notch filter. 100 spectra are averaged, each with an integration time of 800 ms. The measurement is repeated 5 times at three different days leading to an overall of 1500 single spectra. For the imaging measurements, 2000 images were recorded and repeated on three different days. Every image contains two or three droplets of the droplet chain.

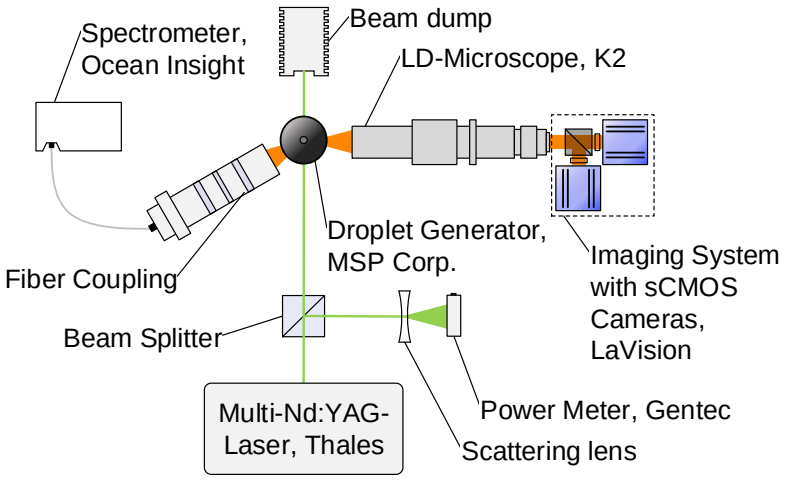


**Fig. 2** Optical setup at the droplet generator.

This setup allows a simultaneous detection of spectral and spatial information and gives clear information on the lasing effects, occurring in the droplets. Thus, a study of the droplet size dependence on the position of the MDR band could be realized. Between 40 µm and 120 µm no change of the MDR spectral region could be observed (not shown here), proving the applicability of the measurement technique.

In the imaging setup, the signal is split by a dichroic mirror and further detected by two cameras. In the post-processing, one image is mapped onto the other via a transformation matrix and a warping algorithm. Using a binarization as displayed in Fig. 3 on the left, the edges and thus the droplets in the pictures are detected and further evaluated. Single droplets are selected as 'useful' or not, according to their size and deformation. Only droplets close to 100 µm with no perceptible deformation are taken into account. With these specifications, a minimum of 12.500 droplets are taken into account for further evaluation. The integrated LIF-signal of the droplet is strongest in its center. This is because of the maximum depth in *z*-direction of the droplet and since the whole droplet is illuminated by the laser beam (thickness of 8 mm). A circular region of interest (ROI) is determined at half of the radius. In this ROI the signal is averaged for both channels and a signal ratio is calculated.

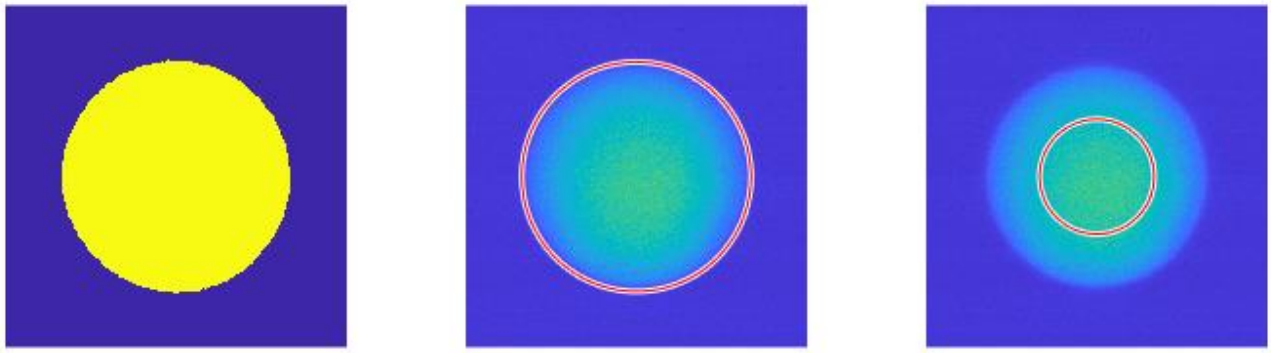

**Fig. 3** Post-processing of the droplet pictures. Left: Binarized droplet image. Middle: Original image with overlay of the detected boundary. Right: Selected ROI at half of the radius.

In addition to the previously described measurements, the mixture of ethanol and both dyes is investigated with an absorption spectrometer (V750, Jasco) in a cuvette. A tempered cuvette holder is integrated in the measuring system, so temperature dependent absorption spectra can be recorded. The absorption measurements were also measured on three different days and averaged in the processing.

## 4. Results

To get a better understanding of the emission process, additional absorption measurements were conducted and the results of the measurements at 293 K and 333 K are depicted in Fig. 4 on the left. Two major peaks at $\lambda \approx 500$ nm and 550 nm can be observed. The first one at shorter wavelengths is due to the absorption of FL and the maximum is significantly higher than the second peak, which is attributed to SRh. This difference in absorption is partly due to the mixture composition of 10:1 (FL:SRh). At higher temperature, the FL peak increases whereas the SRh peak only shows a slight blue shift. The superimposition with the increased FL band leads to this change.

The right graph in Fig. 4 shows the fluorescence emission spectra of the utilized dye mixture at different temperatures, indicating the MDR peak at wavelengths of $\lambda > 640$ nm. Moreover, the combination of the temperature sensitive FL and the temperature insensitive SRh leads to a high sensibility of the fluorescence intensity ratio. For this ratio, two color bands with an optimum high ("blue") and low ("red") temperature sensitivity were elaborated and accordingly the filters for further measurements with an imaging system were selected. These filter regions are hereafter referred to as channel 1 (blue) and channel 2 (red). The range around 532 nm is blocked by the notch filter. The integrated signals under the graph in the shaded regions are applied for the subsequently built signal ratio.

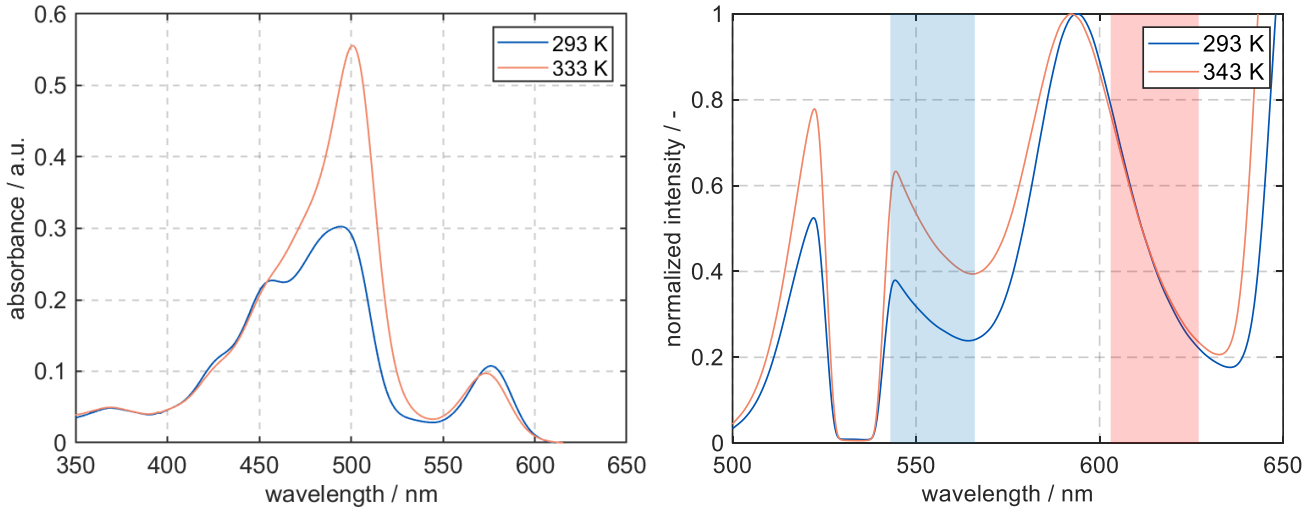


**Fig. 4** Left: Temperature dependent absorption spectrum of FL and SRh dissolved in ethanol. Right: According emission spectrum (exc. with 532 nm). The color channels of the selected filters (based on temperature sensitivity) are marked in blue and red. The signal increase in the region around 650 nm corresponds to the MDR signal.

Examples of the droplets imaged at high resolution through the two spectral channels are shown in Fig. 5 at specific temperatures. On the upper side, the droplet has a temperature of 293 K, in the lower pictures the liquid is tempered to 343 K. Comparing the heated to the non-heated droplet, a significant difference in the intensity change can be seen between both channels. The blue channel (left) shows the increasing signal of FL while only a low intensity change is visible in the emission of SRh in the red channel (right). Recording the droplets only in the restricted wavelength bands, no "ring structures" at the inner droplet surface can be observed. Thus, for droplets in the µm size range, a detection of the MDR can be circumvented by the preceding selection of suitable filters, which is in accordance to the emission spectra presented above.

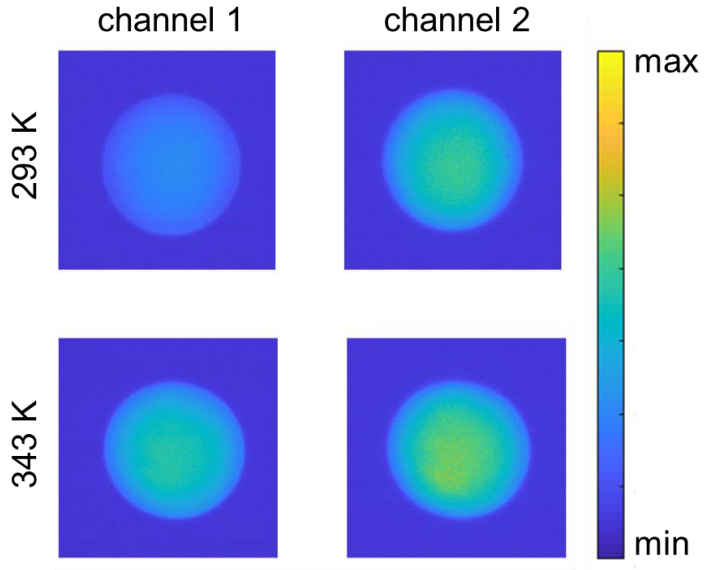


**Fig. 5** Single 100 µm large droplets at 293 K and 343 K viewed through channel 1 ("blue", left) and channel 2 ("red", right column).

Fig. 6 shows the normalized LIF ratios at different temperatures and the resulting linear fit for the measurements with the spectrometer (*s*) and with the cameras in the imaging system (*c*). The slope of the spectrometer calibration curve is steeper than the one of the imaging system. For a direct comparison, the inclusion of the quantum efficiencies of the optical components is missing. By detecting with the imaging system, the filters limit the evaluated channels, whereas these limits are straight theoretical cut-offs in the evaluation of the spectrometer measurements.

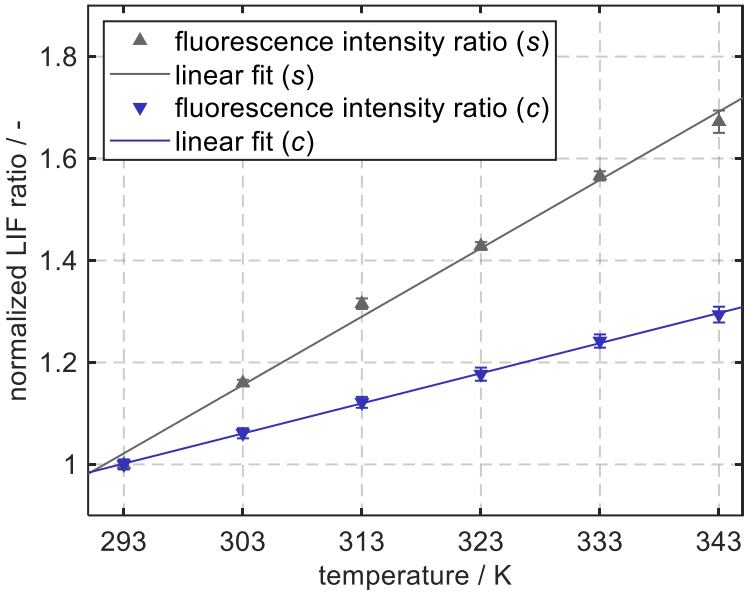


**Fig. 6** Normalized fluorescence intensity ratio of the integrated spectral channels for the measurements with the spectrometer (*s*) and the camera system (*c*) with according standard deviation. The signal ratios are normalized to 293 K.

The slope of the calibration curve for the spectrometer detection describes the resulting sensitivity of 1.34 %/K with a coefficient of determination $R^2$ of 0.995. For the imaging system, a sensitivity of 0.59 %/K with $R^2$ of 0.999 could be realized. In comparison, Chaze et al. (Chaze et al., 2016) and Mishra (Mishra et al., 2016) achieved higher values for the sensitivity, stating values of 2.5 %/K - 3 %/K and 2.39 %/K. However different setups (mm-sized droplets and cuvettes) or liquids were used and no standard deviations are shown for an estimation of the reliability. Much broader color channels were chosen in the previous publications leading to higher differences in the signal ratio and thus a steeper slope. Furthermore, it was mentioned that the temperature insensitive SRh band showed certain fluctuations, which could be due to the reported ring structures in a later work of Chaze et al. (Chaze et al., 2017). As shown in this work, MDR effects can be avoided by selection of according optical filters. Using a dichroic mirror instead of a beam splitter, the signal loss can be counteracted.

## 5. Conclusions

In this work, a successful selection of the two dyes FL and SRh for 2c-LIF measurements in ethanol droplets could be confirmed. First approaches of simultaneous measurements with a spectrometer and two sCMOS cameras on micrometric droplets are reported. The dyes are investigated regarding their different temperature sensitivity. FL shows a strong temperature dependency

while SRh is not affected regarding absorption and emission spectra. The applicability for thermometry measurements was proved with a mixture of both dyes, merely interfering with each other regarding reabsorption effects. Lasing in the droplets was avoided by a proper selection of two optical filters, representing the two color channels for the signal ratios. The simultaneous detection of spectral and spatial information enabled an accurate monitoring and prevented a detection of the MDR effects in the images. Droplet pictures at all measured temperatures were evaluated. A region of interest was defined in which the intensity ratio was determined for the image pairs. The calibration curve of the spectral measurements was compared to the curve of the planar measurements. The sensitivity of planar measurements was lower, than in previous works. This can be explained by the partially weaker signal in the micrometric droplets and the selection of the optical components, which was required to avoid detection of lasing effects. Regardless the lower sensitivity, the replicability of the method is very high and thus applicable for further measurements in droplet chains or technical sprays.
Broader parameter ranges and further post-processing have to be conducted in order to evaluate the difference between the two calibration curves and determine the range of suitable technical applications.

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