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A Fluorescence Approach for Assessing the Composition of Evaporating Droplets

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Accurate measurement of chemical composition is vital for understanding heat and mass transfer mechanisms in two-phase flows like sprays. This letter presents an optical method based on laser-induced fluorescence and fluorescence lifetime measurement. While solvatochromism—shifts in the emission and absorption spectra based on solvent type that alter fluorescence intensity—is well-documented for many fluorescent dyes, fluorescence lifetime offers distinct advantages for two-phase flow applications. Unlike intensity-based methods, lifetime measurements exhibit greater resilience to light attenuation and scattering at liquid/gas interfaces and allow for more flexible detection band selection. The technique leverages the fluorescence lifetime of Eosin Y, which is sensitive to solvent polarity while remaining unaffected by temperature—a crucial feature for systems with fluctuating temperature and composition. We validate this method using acoustically levitated droplets, showing that Eosin Y's fluorescence lifetime can reliably distinguish components in binary mixtures like ethanol/water and isopropanol/water. The high volatility of ethanol and isopropanol causes significant cooling during droplet vaporization, leading to water condensation from the surrounding air. This approach enables detailed analysis of complex evaporation and condensation dynamics.

Heat and mass transfer in sprays have long been subjects of intensive research, given their extensive industrial applications in evaporators, boilers, air condensers, distillation chambers, dryers, combustion engines, and more. Accurately characterizing the transformations that droplets undergo in these processes is challenging, particularly when the liquid contains multiple components with diverse properties. Composition evolves according to transfer phenomena closely related to the droplet dynamics, phase change phenomena (such as evaporation, solidification, and melting), and chemical reactions. Non-intrusive techniques for determining droplet composition would be invaluable for investigating these phenomena; however, despite numerous attempts, no fully satisfactory solution has yet been found¹. For example, Raman scattering spectroscopy encounters difficulties with small, moving droplets due to weak signals and morphology-dependent resonances (MDRs) that distort spectra². Rainbow refractometry shows promise but is limited to perfectly spherical droplets and requires a monotonic relationship between the refractive index and the rainbow angle³. Fluorescence, by contrast, does not face these same limitations and is sensitive to parameters like solvent dipolar moment, hydrogen bonding, pH, and viscosity. Solvatochromism—a phenomenon where the Stokes shift between absorption and emission spectra changes with the solvent—has been documented for numerous dyes, but its practical application in droplet flows has seen limited success due to challenges in using intensity-based measurements in droplet flows. Neglecting reabsorption, the fluorescence signal dF emitted by a small volume dV of liquids, such as a droplet¹, containing the fluorescent molecules, can be expressed as:

$$dF = K \varepsilon \phi C I_0 dV, \quad (1)$$

where I_0 is the laser intensity, C is the dye concentration, ε is the absorption coefficient at the excitation wavelength, and ϕ

is the fluorescence quantum yield (the ratio of emitted to absorbed photons). The parameter K accounts for signal transmission to the detector. Both ε and ϕ depend on solvent properties (viscosity, pH, dipole moment) and temperature¹. Eq. (1) shows that the emitted fluorescence signal is affected by factors undesirable for composition measurements, including droplet size and shape, positioning relative to optics, droplet temperature and signal attenuation due to light scattering from neighbouring droplets. To mitigate some of these effects, the two-color method can be attempted. By selecting two spectral bands for detection and taking the ratio of their intensities, many of the above-mentioned dependencies can be removed or minimized. However, for this method to be effective, two conditions must be met: (1) the spectral bands must respond differently to changes in composition, and (2) the bands must be insensitive to temperature. While condition (1) has been achieved in several studies^{4–6}, the persistent issue of temperature dependence (2) remains unsolved. Additional obstacles for intensity-based measurements is multiple light scattering by droplets which can severely attenuate signal intensity and the presence of small droplets which can be challenging to detect, since fluorescence intensity is roughly proportional to droplet volume^{7,8}. A recent breakthrough in spray measurements has emerged with the application of the Time-Correlated Single Photon Counting (TCSPC) technique to assess fluorescence lifetime (FLT)⁹. When employed effectively, single photon counting provides a dynamic range (maximum signal-to-noise ratio) on the order of 10^6 , in stark contrast to just over 10^2 for intensity-based measurements with conventional instruments. This enhanced capability allows for highly resilient measurements and can be further combined with two-photon excitation to mitigate multiple scattering issues commonly encountered in dense sprays¹⁰.

This letter presents a fluorescence lifetime (FLT) technique

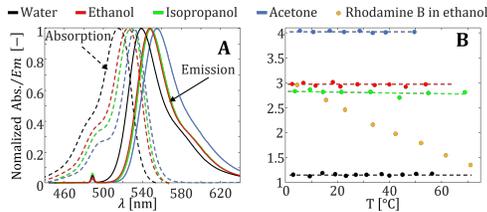


FIG. 1. A) Absorption and emission spectra and B) temperature calibrations of EY dissolved in water ($E_T = 63.1 \text{ kcal.mol}^{-1}$), Ethanol ($E_T = 51.9 \text{ kcal.mol}^{-1}$), Isopropanol ($E_T = 49.2 \text{ kcal.mol}^{-1}$) and Acetone ($E_T = 42.2 \text{ kcal.mol}^{-1}$). E_T is the solvent polarity according to Reichardt scale¹². The temperature variation of rhodamine B when dissolved in ethanol is added in B).

for measuring the droplet composition that is immune to temperature-induced biases. By utilizing FLT, the method is expected to provide robust measurements in spray-like environments. Eosin Y (EY) was evaluated among several fluorescent dyes known for their strong dependence on solvent properties. EY is notably low-cost, non-toxic, and widely available, with applications across diverse fields, making it an even more attractive option. It is soluble in numerous polar and protic solvents, such as water and alcohols. Our observations of EY's absorption and emission spectra across various solvents—such as water, ethanol, Propanol, and acetone (Fig. 1A)—confirm a pronounced variation in Stokes shift with solvent polarity. However, the fluorescence signal cannot be used directly for measuring droplet composition because EY's absorption and emission spectra are highly sensitive to temperature, with intensity variations of approximately 1.6%/K in water¹¹. Although a direct correlation between solvatochromism and fluorescence lifetime (FLT) has not been reported for EY, our extended investigations reveal that EY's FLT is indeed sensitive to solvent polarity in a manner similar to its intensity. Additionally, the FLT remains unaffected by temperature, making EY an excellent candidate for overcoming the challenges of composition measurement under evaporative conditions, where both temperature and composition can vary simultaneously.

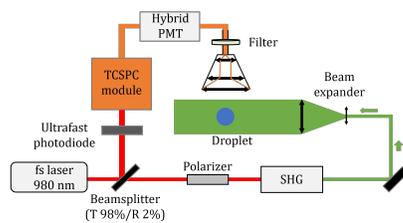


FIG. 2. Setup of TCSPC. A 140 fs pulse from a Ti: Sapphire laser is frequency-doubled to excite EY. Fluorescence is collected with an achromatic doublet and a fast photomultiplier tube. An ultrafast photodiode is used for time reference.

The method employed to characterize the fluorescence decay in the time domain is the so-called time-correlated single-photon counting (TCSPC) technique¹³. Its principle can be compared to a stopwatch, which measures the time difference between an ultrashort laser pulse and the arrival time of fluorescence photons on a subnanosecond scale. A femtosecond Ti: Sapphire laser (Coherent Chameleon Ultra II, tunable from 680 to 1080 nm) generates short light pulses with a width of about 140 fs. To induce the fluorescence of EY, the laser is tuned at 980 nm, and its frequency is doubled using a second harmonic generator from HarmoniXX, APE GmbH (Fig. 2). An objective lens (working distance 90 mm) collects

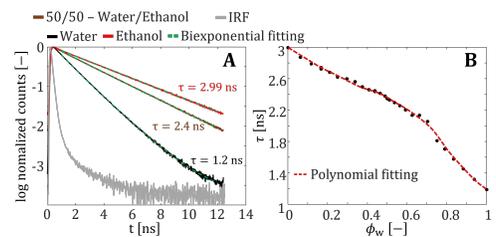


FIG. 3. A) Fluorescence decay of EY when the solvent is pure water, pure ethanol, and a mixture of 50 % in volume of water and ethanol. The instrument response function (IRF) is included for comparison. B) Calibration of the FLT of EY as a function of the water volume fraction in mixtures of water and ethanol.

fluorescence at a right angle from the laser beam and transmits it by an optical fibre to a photomultiplier tube (PMT) (Hamamatsu fast hybrid PMT R10467) for photon counting. A bandpass filter centred on 580 nm with a bandwidth of 20 nm is mounted before the PMT to eliminate unwanted photons from laser light scattering and ambient disturbances. A time correlator (HydraHarp 400 controller, PicoQuant GmbH) which operates at the full repetition rate of the laser (80 MHz) processes the output current of the PMT. It measures the arrival times of individual photons relative to a reference signal provided by an ultrafast photodiode, which receives the laser beam via a beam-splitter. The FLT is evaluated from the fluorescence decay as presented in Fig. 3A). For multi-component mixtures, the time evolution of the fluorescence photon count $N_f(t)$ is well described using a bi-exponential function⁹:

$$\frac{N_f(t)}{N_f(t=0)} = a e^{-t/\tau_1} + (1-a) e^{-t/\tau_2} \quad (2)$$

where parameters a , τ_1 and τ_2 are adjusted from the decay curve employing the least mean square method constraining a between 0 and 1. The average FLT, denoted τ , is defined by:

$$\tau = a \tau_1 + (1-a) \tau_2. \quad (3)$$

The instrument response function (IRF), which represents the time spread introduced by all components in the measurement system, is shown in Fig. 3. The IRF was measured with a full width at half maximum (FWHM) of 90 ps, which is small relative to the fluorescence lifetime, on the order of nanoseconds.

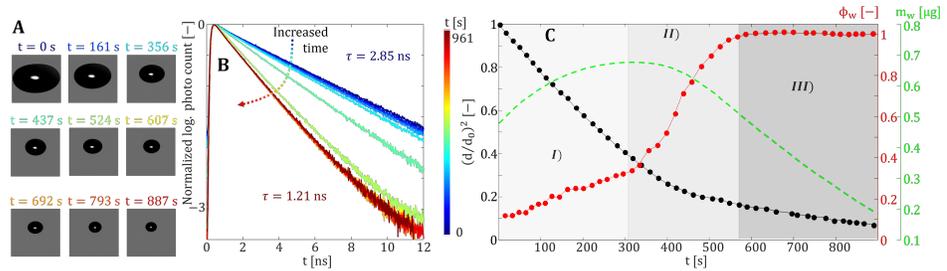


FIG. 4. A) Shadow images of an initially pure ethanol droplet evaporating in ambient air at 19.8°C and a relative humidity of 35%. B) Fluorescence decay at different times of the evaporation process. C) Time evolution of the square normalized diameter, water volume fraction and total water mass as a function of time. The droplet evolution can be divided into three phases: I) Ethanol evaporation predominates, and water condensation occurs concurrently. II) Ethanol evaporation ceases, and water evaporation becomes the dominant process. III) Pure water evaporation.

Nevertheless, the theoretical model in Eq. (2) was refined by convoluting the IRF with the decay model to obtain an unbiased assessment of the parameters a , τ_1 and τ_2 .

A comprehensive investigation of the effects of temperature and solvent composition on the FLT was first conducted in a cuvette for all the selected solvents while changing the liquid temperature. To maintain uniform temperature during the experiments, the solution was continuously stirred. As shown in Figure 1B), the FLT remains constant as the liquid temperature increases by several tens of °C regardless of the solvent. For comparison, the temperature dependence of Rhodamine B dissolved in ethanol is also included in Fig. 1B). It is noteworthy that FLT increases with solvent polarity: τ is approximately 1.1 ns in water, the most polar solvent, and 4 ns in acetone, which is nearly apolar. Table 1 in Supplementary material shows the fluorescence lifetime in various solvents alongside dipole moment, polarizability, dielectric constant, and the empirical ET(30) scale (Reichardt's polarity scale), which is based on the solvatochromism of another dye, betaine. Among these parameters, the ET(30) scale appears to be the most appropriate for describing the behavior of the fluorescence lifetime, followed by the dielectric constant.

The technique was then applied to several mixtures to examine the effect of solvent composition on the FLT. The example of the water/ethanol mixture is described below, while results for the water/isopropanol mixture are provided in the Supplementary Materials as an additional example. In principle, the method for measuring composition can be extended to any binary mixture, as long as the solvents are miscible and the FLT of EY differs significantly between the two components. The fluorescence decay of EY in pure water, pure ethanol and a mixture composed of 50% water and ethanol by volume is presented in Fig. 3A). The composition has a marked effect on the kinetics of fluorescence decay. The decay curves were fitted to determine τ by employing the bi-exponential model in Eq.2. A calibration curve for the effect of composition in ethanol/water mixtures was then obtained by measuring the FLT in the cuvette while gradually adding

water to ethanol and vice versa. The variation of FLT as a function of the water volume fraction ϕ_w is depicted in Fig. 3B). This calibration is essential since the FLT exhibits a non-linear relationship with ϕ_w . The calibration curve in Fig. 3B), whether plotted using mole, mass, or volume fraction, does not show linearity. The polarity of the water/ethanol mixture, which is known to exhibit non-ideal behavior¹⁴, cannot be simply inferred from the proportions of each component in the mixture. In this calibration process, care was taken to limit measurement errors by acquiring a large number of photons (approximately 10 million), conducting measurements at moderate room temperature, covering the cuvette with a lid to prevent component evaporation, and measuring the mass of the solution with a precision balance at each measurement point.

As a validation, the technique was applied to study the evaporation of droplets suspended in an ultrasonic levitator (TEC5 AG). The droplet, composed of a water/ethanol mixture, is positioned in an acoustic standing wave generated between a transducer vibrating at 58 kHz and a curved reflector. A schematic of the levitation system is provided in the Supplementary Materials. The droplet stabilizes a few μ m below a pressure node and is flattened (Fig. 4A) due to the pressure difference between the top and bottom of the droplet. The droplet must be small compared to the half-wavelength of the acoustic field (presently $\lambda/2 \approx 2.8$ mm) to have the acoustic radiation force directed upwards¹⁵. The laser beam was expanded to a diameter of 1 cm to illuminate the entire droplet volume for the FLT measurements. Shadow images are recorded between FLT measurements to monitor the time evolution of the droplet volume. Figure 4 illustrates the evolution of an initially pure ethanol droplet placed in an environment with a relative humidity of 35% and a temperature of 19.8°C. In practice, it takes around 100 seconds to dispense the droplet into the levitator, allow damping of its shape oscillations, and initiate data acquisition. As a result, the composition and size of the droplet have changed slightly by the time of the first measurement, which is designated as the time

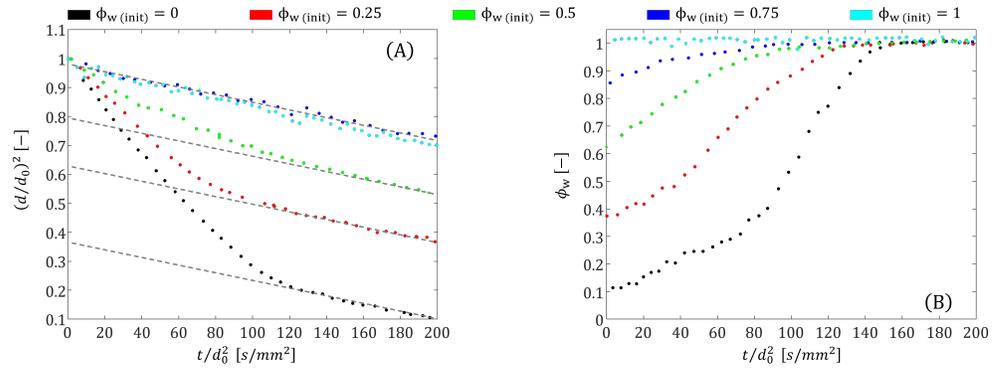


FIG. 5. Time evolution of A) the normalized square diameter and B) the water volume fraction as a function of reduced time. The initial water volume fractions are 0%, 25%, 50%, 75%, and 100%. The ambient temperature is 19.8°C. The relative humidity is 35%. Initial droplet diameters are 1.73, 1.50, 1.66, 1.72, and 1.95 mm, respectively. The dotted lines depicted in A) have the same slope ($K = 1.4 \cdot 10^{-9} \text{ m}^2/\text{s}$). This value is the evaporation rate of a pure water droplet in the experimental conditions.

origin for the results presented. As the droplet progressively evaporates, Fig. 4B) shows that the FLT diminishes progressively from 2.85 ns (corresponding to an initial water volume fraction of 10%) to 1.20 ns, indicative of a pure water droplet. Using the calibration curve presented in Fig. 3B), the volume fraction of water ϕ_w can be evaluated. From literature¹⁶, it is known that the wet bulb temperature of ethanol is as low as 6°C in the air at 19.8°C, meaning that the temperature of a pure ethanol droplet can drop as low as 6°C in the initial stage of evaporation. This low temperature triggers the condensation of the moisture contained in the air (RH=35%) onto the droplet's surface. The total mass of water in the droplet (green curve in Fig. 4 C) can be calculated to evidence this condensation process, knowing the droplet volume from the shadow images and the droplet composition from the FLT measurements. The evolution of the droplet can be divided into three stages:

- I. In the initial stage, ethanol evaporation is intense, and the mass of water increases due to condensation until around 300 s. The square diameter (black points) exhibits a linear decay.
- II. In the second phase (from 300 to 550 s), the evaporation rate decreases sharply as ethanol gets depleted. As observed, the total mass of water (green curve) is decreasing while the water volume fraction (red curve) is increasing indicating that condensation of water has stop and is progressively replaced by water evaporation.
- III. In the last stage (from 550 to 900 s), the droplet is only composed of water. The square diameter decreases linearly with time but with a slope much smaller than during the first stage. The evaporation is governed by the so-called d^2 -law¹⁷, which implies a quasi-steadiness of temperature and composition for the droplet.

Finally, our investigations were extended to cover a range of initial water volume fractions from 0% to 100%. The time evolution of the normalized square diameter $[d/d_0]^2$ and the water volume fraction ϕ_w are presented in Fig. 5. By dividing the time t and the square diameter d^2 by the square initial diameter d_0^2 in the x and y axes, respectively, we enable a better comparison of experiments where the initial diameter d_0 differ. As expected, the first stage of the droplet evolution, dominated by ethanol vaporization, becomes shorter as the initial water volume fraction is increased. Accurate measurements of the water volume fraction allow to clearly identify the moment when the droplet consists solely of pure water. After the ethanol is depleted from the droplet, the same slope of d^2 is observed since the evaporation rate is only a function of the sound pressure level in the acoustic levitator and the ambient conditions (temperature and humidity) for a pure liquid droplet¹⁸. The precision of the FLT measurements has been estimated at 0.04 ns, which corresponds to an uncertainty in the water volume fraction of approximately $\pm 4\%$ based on Figure 3B. A similar level of uncertainty is maintained for the water/isopropanol mixture, as detailed in the supplementary materials.

An optical technique has been developed to measure the composition of multicomponent mixtures in sprays and, more broadly, in two-phase flows. Validation tests in a temperature-controlled cell demonstrated that this method can accurately determine composition independently of temperature, which is a major advantage when both composition and temperature change simultaneously. Although Fluorescence Lifetime (FLT) is an absolute quantity, preliminary calibration measurements are required to correlate the volume fraction of the components to the FLT. The technique was tested on acoustically levitated droplets composed of ethanol/water and isopropanol/water mixtures as a proof of concept. As the more volatile components, ethanol and isopropanol, evaporate, the

temperature of the droplet decreases causing the condensation of water from the surrounding moist air. This complex interplay of evaporation and condensation gradually ends when ethanol or isopropanol are depleted, leaving only pure water that evaporates more slowly. Our composition measurements showed strong correlation with changes in the slope of the squared diameter, further validating the method. The measurements proved to be robust and capable of accurately capturing changes in volume fraction. In the acoustic levitator, the experimental conditions allow for an acquisition rate of fluorescence photons of at least 10^5 cps, while background and sensor noise remain low at around 50-70 cps. Each measurement was terminated once 1 million photons were accumulated. The uncertainty in FLT measurements is estimated to be around 0.04 ns, which, according to the calibration curve (Fig. 3B), corresponds to an uncertainty of approximately $\pm 1\%$ to $\pm 3.2\%$ for the volume fraction of the components. The techniques has been designed with optically dense sprays in mind. With an excellent signal-to-noise ratio of around 10^4 , it can undoubtedly handle more challenging conditions, where light scattering and absorption can pose significant challenges to intensity-based measurements. Extending the technique to more complex mixtures seems feasible, provided that the FLT of EY differs sufficiently across the various compounds.

SUPPLEMENTARY MATERIAL

See supplementary material for supplementary information.

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DATA AVAILABILITY STATEMENT

Data available on request from the authors

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