# Fluorescence lifetime measurement for studying evaporation of bi-component droplet

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ABSTRACT

Sprays play a crucial role in engineering applications such as evaporators and combustion chambers. Predicting the evaporation of multi-component liquid droplets is complex due to the changing composition and properties over time. Measuring droplet composition is challenging, with limited non-intrusive methods available. Raman spectroscopy is widely used for composition measurement, though it faces hurdles like weak signals and interference from morphological resonances. Laser-Induced Fluorescence (LIF) offers another approach but often requires optical models to interpret data due to varying droplet size and position. Fluorescent dyes can be added to liquid mixtures for composition analysis, but fluorescence intensity is highly sensitive to temperature, complicating measurements. Fluorescence lifetime measurements offer a promising alternative. Unlike intensity, fluorescence lifetime is an absolute quantity, less affected by reabsorption. This study aims to develop a novel method using fluorescence lifetime to analyze droplet composition, leveraging Time-Correlated Single Photon Counting (TCSPC) for precise measurements. Factors affecting measurement accuracy, such as dye concentration, solvent polarity, and temperature sensitivity, are thoroughly investigated. Calibration curves are established for binary mixtures, specifically ethanol-water, to correlate fluorescence lifetime with volume fraction. Experimental setups utilizing TCSPC and femtosecond lasers for dye excitation are detailed. Results demonstrate that fluorescence lifetime decreases linearly with solvent polarity and is influenced by temperature and dye concentration. High dye concentrations lead to self-quenching, altering temperature sensitivity. The developed method was applied to study the evaporation of ethanol-water droplets under acoustic levitation. Findings indicate that evaporation rates slow down as the water fraction increases, with initial measurements showing higher water content due to partial evaporation during droplet stabilization. This research introduces a novel technique for droplet compositional analysis using fluorescence lifetime, providing insights into optimizing measurement accuracy. The method's application to evaporative studies showcases its potential for advancing understanding in engineering and related fields.

## 1. Introduction

Sprays are crucial in engineering, used in processes like evaporators and combustion chambers. When dealing with liquid droplets made up of multiple components, predicting their evaporation becomes complex. The composition and properties change over time due to varying volatility, creating concentration gradients. The measurement of droplet composition presents a formidable task, with limited non-intrusive methods available. Among the techniques employed, Raman spectroscopy stands out as one of the most widely utilized methods for composition measurement. This spectroscopic approach relies on studying the frequency shift of light, offering valuable insights into the composition of liquid droplets. However, it is essential to acknowledge potential hurdles, such as weak signals and interference from morphological resonances, which can impact the accuracy and reliability of the measurements.

Laser-Induced Fluorescence (LIF) is also a useful method for characterizing the chemical composition of liquid mixtures. In some cases, fluorescent molecules naturally present in the mixture can be used for this purpose. (Maqua, Depredurand, Castanet, Wolff, Lemoine, et al., 2007) employed LIF to study the vaporization of ethanol/acetone droplets. Acetone molecules fluoresce in the UV range, unlike ethanol molecules. As the droplets vaporize, the fluorescence intensity gradually decreases due to the higher volatility of acetone compared to ethanol. Interpreting these measurements required developing an optical model that accounted for the droplet size, position relative to the optics, and light absorption, which plays a significant role at high molar fractions of acetone.

Another approach to characterizing composition is by adding a specific dye to the liquid mixture, typically at a concentration of a few $\mu$g/L. The polarity, viscosity, and chemical interactions of the liquid solvent can affect the emission and absorption of fluorescent dyes. In multiphase flows where moving liquid interfaces can perturb the fluorescence signal, a ratiometric method is necessary. These measurements are conceptually similar to temperature measurements using fluorescence ratios. (Coppeta & Rogers, 1998) pioneered pH measurements in aqueous solutions using a two-color approach. They used a pair of dyes (fluorescein and rhodamine B) with emission spectra shifted in wavelength to obtain detection bands with distinct responses to pH. However, they reported potential issues in their measurements, such as bias due to reabsorption, especially in the case of pH-dependent fluorescein. Recently, (Koegl et al., 2020) suggested using two-color LIF to characterize the composition of n-decane/butanol blends. They observed significant changes in the absorption and emission spectra of the Nile Red dye with varying volume fractions of butanol. However, the emission spectrum of Nile Red is also strongly sensitive to temperature, making it challenging to separate the effects of temperature and composition. Consequently, the

fluorescence ratio can be used to determine the butanol concentration when the temperature is held constant. In a similar vein, (Maqua, Depredurand, Castanet, Wolff, & Lemoine, 2007) developed a method based on three spectral detection bands in a study of ethanol/acetone droplet evaporation. These bands were used to calculate two intensity ratios with different sensitivities to temperature and composition. By analyzing the variations in these two ratios, (Maqua, Depredurand, Castanet, Wolff, & Lemoine, 2007) were able to infer both temperature and composition. However, the accuracy of composition measurements was limited due to the detection bands were more sensitive to temperature than composition. Identifying suitable detection bands in ratiometric methods can be a complex and time-consuming task. As an alternative, fluorescence lifetime measurements can be employed. Unlike intensity, fluorescence lifetime is an absolute quantity. It is possible to measure the composition of binary mixtures using a single detection band and a single fluorescent dye. Reabsorption is expected to have minimal impact on lifetime measurements as long as secondary emissions of photons induced by reabsorption remain negligible. While a few studies, such as (Mendels et al., 2008), have used fluorescence lifetime to measure composition in the field of fluid mechanics, they did not extensively investigate the effects of temperature on their measurements or the consequences of dye enrichment. However, in the case of droplet evaporation, both temperature and dye concentration are likely to vary significantly. The primary aim of the current study is to develop a novel measurement technique for compositional analysis using fluorescence lifetime as a key parameter. This research delves into a comprehensive exploration of various factors that may influence measurement precision. Factors under scrutiny include the temperature sensitivity of the dye, the impact of dye concentration and the influence of solvent's polarity on the fluorescence lifetime. Through a systematic investigation, this study seeks to uncover valuable insights into optimizing the accuracy and reliability of composition measurements. The method will be then used to study the evaporation of bi-component droplet under acoustic levitation.

## 2. Experimental setup

Time Correlated Single-Photon Counting method (TCSPC) is used here to measure the fluorescence lifetime. The experimental setup presented in Fig. 1 is similar to a previous study by (Mehdi et al., 2021), where the fluorescence lifetime was used for measuring the temperature of water droplets injected into a polydisperse spray. The photoexcitation of the fluorescent dye is performed by means of a femtosecond Ti:Sa laser (Coherent Chameleon Ultra II). The laser has a pulse width of about 140 fs and its emission wavelength can be tuned from 690 to 1080 nm. For an excitation in the visible range, the frequency of the laser beam is doubled using a second harmonic

generator (HarmoniXX from A·P·E GmbH). A hybrid photomultiplier tube (R10467, Hamamatsu) cooled by a Peltier cell is used to detect the fluorescence photons. The output current of the photomultiplier is transmitted to a time-correlating counter (HydraHarp 400 controller, PicoQuant GmbH) which is operating in forward start stop mode to determine the arrival times of the photons. These measurements require a sharp timing of the laser pulse emission, which is achieved using a fast photodiode (TDA 200 from PicoQuant GmbH), which is also connected to the timing electronics. This photodiode receives the laser light reflected by a beam splitter (99% T, 1% R) positioned at the laser output. The time difference between the event and the detection of a photon by the photomultiplier tube (PMT) is recorded in a histogram that displays the number of the photons as function of time. A bandpass filter is mounted in front of the photomultiplier tube to limit perturbations due to the ambient light. When necessary, this filter is changed to match the emission of the fluorescent dye. As an example, Fig. 3 shows the fluorescence decay on the spectral band [570 nm-590 nm] of Eosin Y (EY) dissolved in various solvents (acetone, ethylene glycol, ethanol, and water) when excited at 520 nm. The fluorescence decay is much faster in water which is the solvent with the highest polarity. The fluorescence lifetime of EY gets shorter as the solvent polarity.

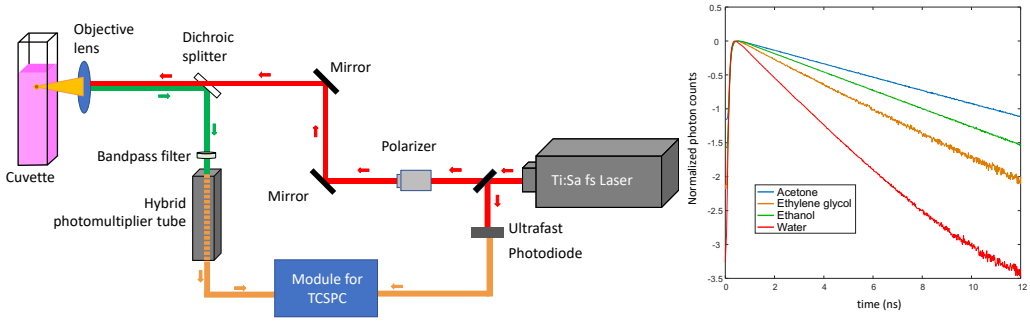


**Figure 1:** a) Experimental setup used to measure the fluorescence lifetime of the dyes b) Fluorescence decay of Eosin Y in various solvents. These measurements were obtained in a cuvette at room temperature ($C_{EY}$=$10^{-6}$ mol/L, $T$ =20°C using a band pass filter, [570 nm-590 nm]).

The fluorescence lifetime τ is defined as the time that fluorescent molecules remain in the excited state before returning to the ground state. It is commonly assumed that the fluorescence decay follows a mono-exponential decay. However, to obtain a better fit, it was shown in (Mehdi et al., 2021) that the fluorescence decay is usually better described by a bi-exponential function. The fluorescence decay is then described as follows:

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

where $a$ is an average parameter between 0 and 1. From Eq. (1), the fluorescence lifetime τ is computed as:

$$\tau = a\tau_1 + (1 - a)\tau_2, \quad (2)$$

This value of the lifetime can be viewed as the lifetime a fluorophore with a monoexponential decay which would have the same steady-state fluorescence intensity $\left(F_\infty = \int_0^\infty F(t)\, dt\right)$. When the solvent is a mixture of two chemical species, considering a two-exponential decay is essential. In practise, parameters, $a$, $\tau_1$ and $\tau_2$ are obtained by a non-linear least squares method, consisting to minimize the difference between the theoretical decay given by Eq. (1) and the experimental decay (Mehdi et al., 2021). Since the fluorophore interacts with both solvent species and its lifetime differs in each of them, the decay must be at least a combination of two exponentials. However, despite a two-exponential fitting greatly improves the quality of the fit compared to a one-exponential decay, adjusted values of parameters $\tau_1$ and $\tau_2$ cannot be easily related to the lifetimes of the fluorophore in the two-solvent species, nor does the parameter $a$ can be identified to the mole fraction of the binary mixture.

The accuracy of the valuation of τ depends on several factors. Firstly, the timing jitter of the different elements that constitutes the TCSPC system may induce a bias in the measurement. The instrument response function (IRF), i.e. the time spread introduced by all the components in the measurement system, was evaluated at 90 ps width at half maximum (FWHM). This is small in comparison to the fluorescence lifetime. Nevertheless, the theoretical model in Eq. (1) is convoluted to the IRF, before the parameters $a$, $\tau_1$ and $\tau_2$ are estimated. The noise coming from the PMT and the environment is considered by adding a "noise" uniformly distributed in time to the fluorescence model. The TSCPC technique is remarkable for its high signal to noise ratio. The noise (count rate in the dark) is about 70 Cps while the count rate is usually about 105-106 Cps in the measurements. This enables to capture without difficulty variations over more than 3 decades in the recorded histograms, provided that enough photons are collected.

**3. Effect of the solvent**

The fluorescence lifetimes of the dyes were measured in various solvents, and the measurement for Eosin Y is presented in Fig. 2. As we have previously discussed, the effects of solvents on fluorescence do not have a definitive explanation. However, in certain cases, the dominant factors such as polarity or viscosity can be identified. Nonetheless, a few general observations can be made. Firstly, it is noteworthy that the fluorescence lifetime is often longer in aprotic solvents like acetone and 3-pentanone. Conversely, in protic solvents, particularly water, as well as bi and tri

alcohols, the fluorescence lifetime is generally lower. The fluorescence lifetime of EY and Oxazine 4 appears to decrease with increasing solvent polarity. This behaviour is depicted in Fig. 2, where it can be observed that the fluorescence lifetime of EY decreases approximately linearly with the polarity scale ET(30). Many fluorescent dyes are suitable for determining composition when the solvent species have significantly different polarities, such as water/acetone. However, when the polarity of the mixture compounds is similar, such as ethanol/isopropanol or ethylene glycol/glycerol, it becomes challenging to use fluorescence lifetime to detect changes in composition.

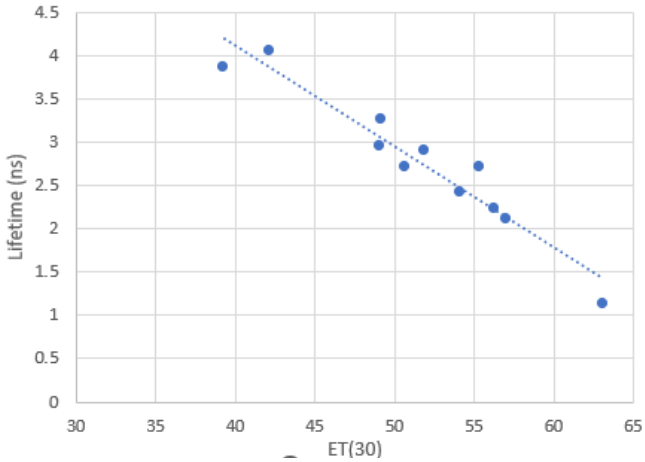


**Figure 2:** Effect of the polarity coefficient ET(30) on the fluorescence lifetime of Eosin Y

## 4. Effect of the temperature

The impact of temperature on fluorescence lifetime is a crucial concern in evaporative systems where heat and mass transfers occur simultaneously. To investigate this effect, lifetime measurements were conducted using a 50 mL glass cuvette equipped with an immersed heating resistor. A PID controller connected to a thermocouple enabled the adjustment of power supplied to the resistor, allowing the desired temperature to be achieved in the cuvette. For the sake of brevity, the presented results focus on a limited number of cases. Fig. 3 illustrates the temperature effect on various fluorescent dyes in water. Among the dyes tested, Rhodamin B and PM556 exhibit the highest sensitivity to temperature in water. The temperature-dependency of Rhodamin B fluorescence quantum yield is commonly attributed to the flexibility of the diethylamino groups located on its xanthene core, which accelerates non-radiative internal conversion (Casey & Quitevis, 1988). To the best of our knowledge, the effect of temperature on PM556 has not been previously reported. The temperature effect on other dyes is relatively minor. A decrease in the

fluorescence lifetime of Ox4 and an increase in the fluorescence lifetime of EY can be observed when the temperature varies by several tens of degrees Celsius. Similar trends were observed in other solvents.

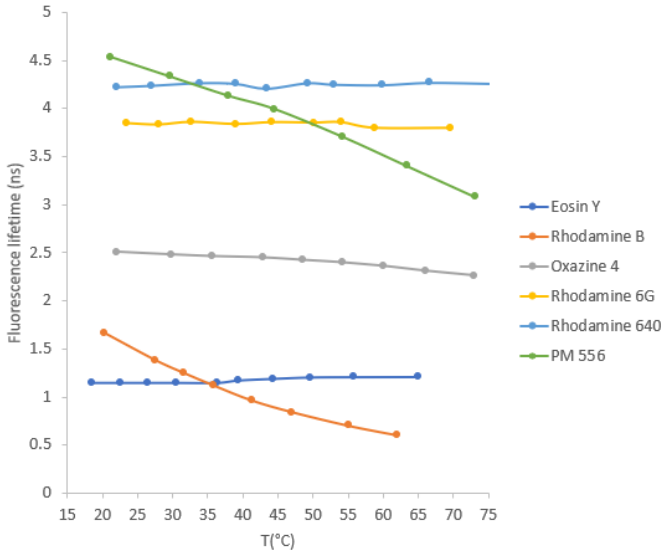


**Figure 3:** Influence of temperature on the fluorescence lifetime of the dyes in water. The dye concentration was set at $10^{-5}$ mol/L. Measurements were performed using deionized water at initial pH=6.5 at 20°C.

## 5. Effect of the concentration

An additional crucial consideration is the impact of dye concentration. During the evaporation of the liquid solvent, the concentration of the dye can substantially increase as the dye molecules remain in the liquid phase. However, it is anticipated that the fluorescence lifetime remains unaffected by the dye concentration within a specific range where the fluorescent molecules do not chemically or photonically interact. To demonstrate this phenomenon, a microscope objective was employed, and two-photon excitation of the fluorescence was carried out. The two-photon fluorescent spot was deliberately positioned in close proximity to the edge of the glass cell. Additionally, to minimize the contribution of secondary fluorescence, photon detection was conducted within a spectral band that is not subject to reabsorption. Detailed measurements for Eosin Y, Rhodamine 6G, and Rhodamine B can be found in Fig. 4.

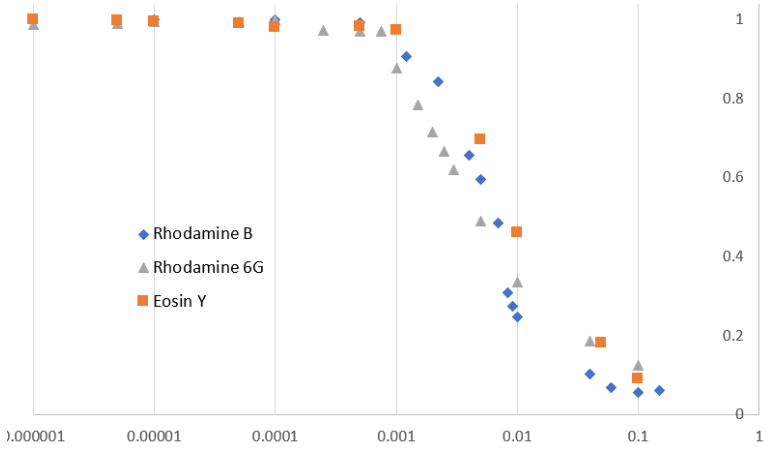


**Figure 4:** Evolution of the fluorescence lifetime of Rhodamine B, Rhodamine 6G and Eosin Y as a function of the concentration of the fluorescent molecule in water. Values are normalized by the fluorescence lifetime $\tau_0$ at low concentration.

As the concentration approaches 10-3 mol/L, a significant decline in fluorescence lifetime is observed, attributed to self-quenching. This phenomenon occurs when energy is transferred to another fluorescent molecule without involving emission and reabsorption of photons.
When the distance between fluorescent molecules approaches the Forster distance, a notable reduction in the temperature dependence of fluorescence lifetime is observed, particularly in the case of RhB. This effect is depicted in Figure 5. The temperature sensitivity of RhB primarily arises from collisional de-excitation with solvent molecules and energy dissipation due to local viscosity. However, at high concentrations, these non-radiative deactivation pathways are superseded by energy transfer to other fluorescent molecules (self-quenching). As a result, the sensitivity of fluorescence lifetime to temperature undergoes modification.

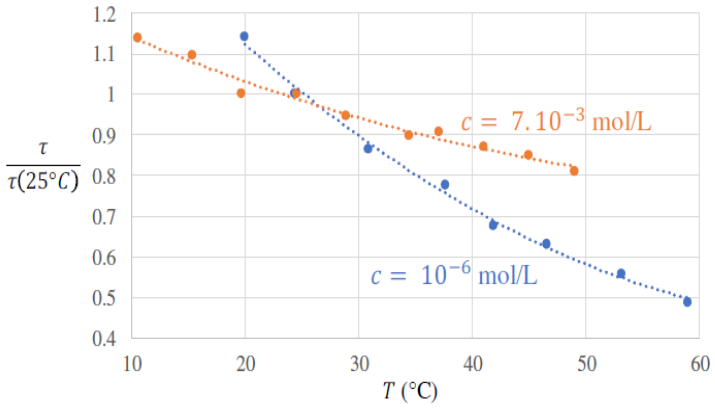


**Figure 5:** Evolution of the fluorescence lifetime of RhB dissolved into water at two concentrations $c = 10^{-6}$ mol/L and $c = 7 \times 10^{-3}$ mol/L.

## 6. Calibration of the mixing fraction

To ascertain the droplet composition accurately, the implementation of a calibration curve is imperative, establishing a correlation between the volume or mass fraction of the mixture and the corresponding fluorescence lifetime value. This calibration procedure is executed within a dedicated cell. This investigation concentrates on the binary mixture of ethanol/water, with intentions to broaden the scope to encompass additional binary mixtures in the future. The calibration process is initiated by introducing an initial volume of water, followed by incremental additions of ethanol. Following each ethanol addition, the solution undergoes thorough stirring, and the resulting fluorescence lifetime is recorded. To ensure accuracy, a precision weighing scale is employed to precisely determine the mass of ethanol introduced at each step. Subsequently, both mass and volume fractions are meticulously calculated. Fig. 6 represents the evolution of the fluorescence lifetime as a function of the volume fraction of water.

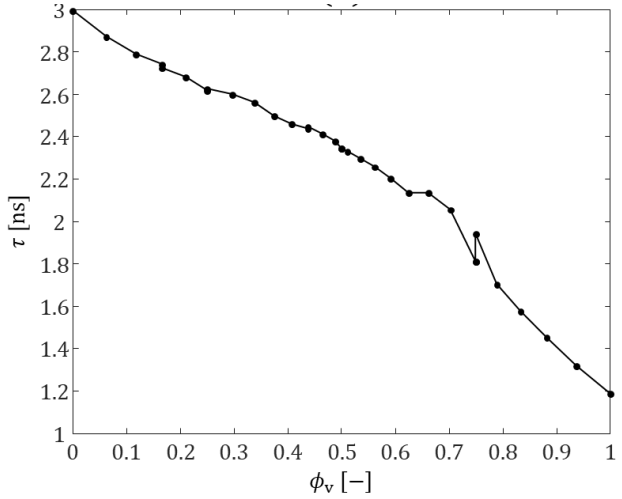


**Figure 6:** Calibration of the volume fraction measurements for water/ethanol mixture.

As observed, there is no linear relationship between the fluorescence lifetime and the volume fraction. For low water mixtures, the variation of the fluorescence lifetime with the volume fraction is generally less important. In practice, this means a lower accuracy in the measurement of the mixture fraction. The calibration curve is fitted using a sixth order polynomial law using the least squares method:

$$f_v = -3493\,\tau^6 + 4.604\,\tau^5 - 24.48\,\tau^4 + 67.04\,\tau^3 - 99.67\,\tau^2 + 75.94\,\tau - 22.11$$

The calibration is then used to asses the evolution of wate/ethanol droplet evaporation under acoustic levitation.

## 7. Evaporation of ethanol/water droplet under acoustic levitation

The acoustic levitator consists of a transducer and a concave reflector. The transducer is attached to a piezoelectric crystal that vibrates at a frequency of 58 kHz. The distance between the

transducer and the reflector is adjusted with a micrometer in order to maintain a standing wave. The droplet stabilizes in the acoustic field at a position slightly below a pressure node. The pressure difference between the top and the bottom of the droplet generates a force that overcomes gravity keeping the droplet suspended. This differential pressure tends to flatten the droplet, which takes an oblate spheroid shape. The curved shape of the reflector helps to concentrate the acoustic wave in the center of the levitator, which generates a radial pressure gradient. This radial gradient is much smaller than in the vertical direction but is sufficient to maintain millimeter sized drops on the vertical axis of the levitator.

In practice, the room temperature and the relative humidity are recorded by sensors before, during and after the experiments. This ensures that ambient conditions are steady during the measurement. Values of the ambient temperature and relative humidity are expected to be determined with a respective accuracy of ±1°C and ± 1%. The initial droplet volume is not precisely controlled, as it depends on the droplet detachment from the syringe needle. The estimation of the SPL is obtained from shadowgraphy measurement of the droplet taken a few seconds after the droplet has been placed in the levitator. If the composition and temperature have not changed, the density and surface tension of the liquid mixture are known with a good accuracy. The method developed by Yarin et al. can be used to estimate the SPL based on the aspect ratio and volume of the droplet.

Evaporation study of water/ethanol mixture were made under the conditions summarized in Table 1. Fluorescence lifetime measurement were coupled with shadowgraphy measurement in order to gain information about the droplet size over time.

**Table 1** Experimental conditions for the study of droplets made up of water/ethanol mixtures of different initial volume fraction of water

| $\boldsymbol{Water\ initial\ volume\ fraction\ f_v}$ | $\boldsymbol{d_0}$ $\boldsymbol{[mm]}$ | $\boldsymbol{T_{amb}}$ $\boldsymbol{[°C]}$ | $\boldsymbol{RH}$ [%] | $\boldsymbol{Axis\ ratio}$ | $\boldsymbol{SPL}$ $\boldsymbol{[dB]}$ |
|---|---|---|---|---|---|
| 1 | 1.95 | 19.8 | 35 | 1.41 | 161.3 |
| 0.75 | 1.72 | 21.6 | 41 | 1.35 | 161 |
| 0.5 | 1.66 | 19.8 | 35 | 1.58 | 161.4 |
| 0.25 | 1.50 | 20.9 | 41 | 1.32 | 161.3 |
| 0 | 1.73 | 21.3 | 41 | 1.27 | 163.6 |

The time evolution of the normalized square diameter $(d/{d_0}^2)$ and that of the water volume fraction as a function of the reduced time $t/{d_0}^2$ have been shown, where $d_0$ is the diameter of the droplet at the time origin $t = 0$ (corresponding to the first measurement point). As expected, the evaporation rate slows down considerably as the amount of water initially present within the

droplet is increased. Measurements show that there is systematically a higher value of the water volume fraction at $t$=0 (first measurement point) than in the mixture which was prepared prior to the experiment. This can be explained by the fact that it takes about 30 s to insert the droplet inside the levitator, stabilize it (as there is an oscillation phase after the droplet detachment), then adjust the SPL and the droplet position relative to the optics. During this period, which is difficult to reduce, the droplet has already partially evaporated, and its composition has evolved towards a higher volume fraction of water. It has to be noted that a droplet of pure ethanol is progressively transformed into a pure water droplet. This is due to the condensation of the water moisture contained in the air ($RH = 35\%$).

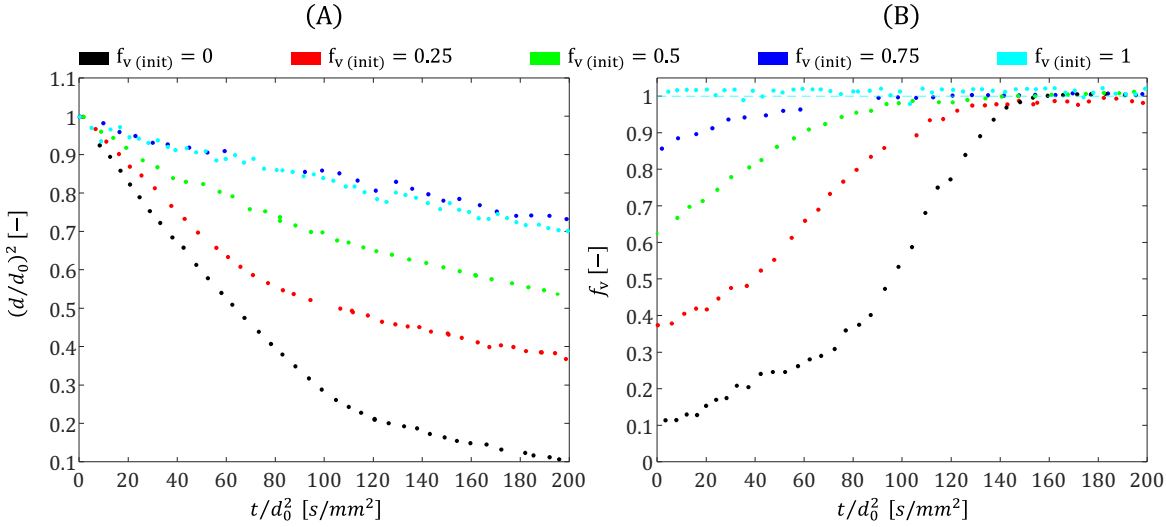


**Fig. 7:** Time evolution of the A) normalized square diameter $(d/d_0)^2$ and B) the volume fraction of water as a function of the reduced time $t/d_0^2$ for the experimental conditions summarized in Table 1.

## 8. Conclusions

In conclusion, the study presented here addresses the challenges associated with characterizing the composition of liquid droplets, particularly in the context of evaporative processes. Various methods, such as Raman spectroscopy, Laser-Induced Fluorescence (LIF), and fluorescence lifetime measurements, have been explored for their efficacy in providing insights into droplet composition. While each method has its strengths and limitations, the focus of this research lies in developing a novel technique using fluorescence lifetime as a key parameter. The investigation delves into the factors influencing measurement precision, including the effects of temperature, solvent properties, and dye concentration. The use of Time Correlated Single-Photon Counting (TCSPC) method for fluorescence lifetime measurements is detailed, emphasizing its high signal-to-noise ratio and suitability for accurate measurements. The impact of solvent properties, temperature, and dye concentration on fluorescence lifetime is thoroughly examined. The findings

reveal trends such as the linear decrease of fluorescence lifetime with solvent polarity and the sensitivity of certain dyes to temperature variations. Additionally, the study underscores the importance of considering self-quenching effects at higher dye concentrations. To practically apply the developed technique, a calibration curve is introduced to correlate fluorescence lifetime with the volume fraction of a binary mixture. This calibration process is crucial for accurately determining droplet composition, as demonstrated in the study of ethanol/water mixtures under acoustic levitation. This research not only introduces a novel approach for compositional analysis using fluorescence lifetime but also provides a comprehensive understanding of the factors affecting measurement accuracy. The practical application of this technique in the study of evaporative processes showcases its potential significance in engineering and related fields.

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