# REMTES

# TECHNOLOGY FOR REMOTE TEMPERATURE MEASUREMENTS IN MICROFLUIDIC DEVICES

PROGRAM-PRIZMA-2023-2026
Grant Agreement: 7017

## Deliverable 2.2.

## Report on luminescence thermometry measurements in microfluidic luminescent probes

**Version Final**

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# INTRODUCTION

**REMTES – “Technology for remote temperature measurements in microfluidic devices”** is a Science Fund of the Republic of Serbia funded project (Program PRIZMA, Grant Contract No. 7017) coordinated and completely executed by "Vinča" Institute of Nuclear Sciences – National Institute of the Republic of Serbia, University of Belgrade (VINS). The project will run from December 1st, 2023, to November 30th 2026.

REMTES is a highly ambitious and innovative project aimed at developing a breakthrough system for measuring sample temperatures on the nanoliter scale. The project will develop an optical self-referencing thermometer for use in micro- and nanofluidics in the 0–100 °C temperature range by exploiting temperature-induced changes in the luminescence of materials and nanomaterials; that is, by advancing luminescence (nano-) thermometry in a targeted manner. The project aims to go beyond the state of the art and implement a radically new technology that merges the fields of luminescence thermometry, photothermal spectroscopy, and microfluidics to develop new-generation luminescent thermometry probes using cutting-edge luminescent, temperature-sensitive, and chemically stable inorganic materials in bulk and nanomaterial forms. The probes will be embedded in microfluidic chip channels to enable self-referenced remote temperature measurements, and the technology will be validated by a portable microfluidic luminescent thermometer, as well as in-situ temperature measurements of fluid flow in nanoliter volume samples. Multiple conceptual breakthroughs can be further envisaged from the proposed technology credibly spreading its impact to multiple technological areas.

**D2.2: Report on luminescence thermometry measurements in microfluidic luminescent probes** is a deliverable of WP2 of the REMTES project. The report the thermometry properties (absorption, excitation, steady state and time-resolved emissions, q, Sr, thermal stability, reproducibility of temperature readout) of the microfluidic luminescent thermometers containing a microfluidic chip with an integrated luminescence probe developed in subactivity 3.3. A maximum of two microfluidic luminescent probes will be selected for technology validation.

# D3.3.: Report on luminescence thermometry measurements in microfluidic luminescent probes

In this phase of the project, the fabricated microfluidic luminescence probe (MLP), presented in detail in Deliverable D3.3 Fabrication of a Microfluidic Luminescence Probe, was tested for temperature measurements using two approaches: the traditional luminescence intensity ratio (LIR) method and a Principal Component Analysis (PCA)–based method.

## Temperature-dependent photoluminescence measurements

In Figure 1 temperature-dependent luminescence spectra of microfluidic luminescence probe with $RbY_3F_{10}$: 10mol%Ce, 20mol%Tb are presented. From obtained results thermometric parameters of the probe were analyzed by two approaches: the traditional luminescence intensity ratio (LIR) method and a Principal Component Analysis (PCA)–based method.

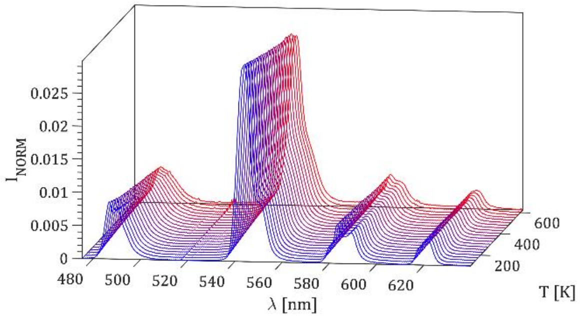

**Figure 1** Temperature-dependent photoluminescent spectra of microfluidic luminescence probe with $RbY_3F_{10}$: 10mol%Ce, 20mol%Tb.

The most significant thermometric parameters that refer to the quality and potential use of thermometers: relative and absolute sensitivity ($S_R$ and $S_A$), average accuracy (ΔT, the mean value of the difference between the measured and nominal temperature values), and precision (δT, standard deviation of the Ti(T) distribution) can be calculated using the following equations:

$$S_A = \left|\frac{dQ}{dT}\right|; \; S_R = \left|\frac{100\%}{Q}\frac{dQ}{dT}\right|$$

$$\Delta T(T) = \frac{1}{N_{VAL}}\sum_{i=1}^{N_{VAL}}\left(T - T_i(T)\right) = T - \frac{1}{N_{VAL}}\sum_{i=1}^{N_{VAL}} T_i(T) = T - \overline{T_i(T)}$$

$$\delta T(T) = \sqrt{\frac{1}{N_{VAL}-1}\sum_{i=1}^{N_{VAL}}\left|T_i(T) - \overline{T_i(T)}\right|^2}$$

## Luminescence intensity ratio (LIR) approach

Luminescence intensity ratio read-out is the most popular approach in luminescence thermometry. In Boltzmann-type luminescence thermometry, lanthanide ions with two thermally coupled emitting levels, Level 1 and Level 2, with energy separation ΔE, and emission from both levels are excited. At low temperatures emissions from the lower level dominate with only small emissions from the upper level. With temperature increase the upper level becomes more populated and its emission increases relative to the emission from the lower level. In ratiometric analysis, the ratio of emission intensities from upper and lower levels is the measure of temperature.

When emissions from adjacent thermalized excited levels are utilized (Boltzmann thermometers), the LIR can be explained by the Boltzmann distribution [5]:

$$LIR = \frac{I_H}{I_L} = Be^{-\frac{\Delta E}{kT}},$$

where $I$ represent the integrated intensities from higher ($H$) and lower ($L$) energy levels, $\Delta E$ is the energy difference between the excited levels, $B$ is the temperature invariant host-dependent constant, and $k = 0.695\ \mathrm{cm^{-1}K^{-1}}$ is the Boltzmann constant. Based on this, absolute (Sa - blue line) and relative (Sr - black line) sensitivities, average accuracy (ΔT – blue diamonds), precision (δT – black circles) were calculated and presented in Figure 2.

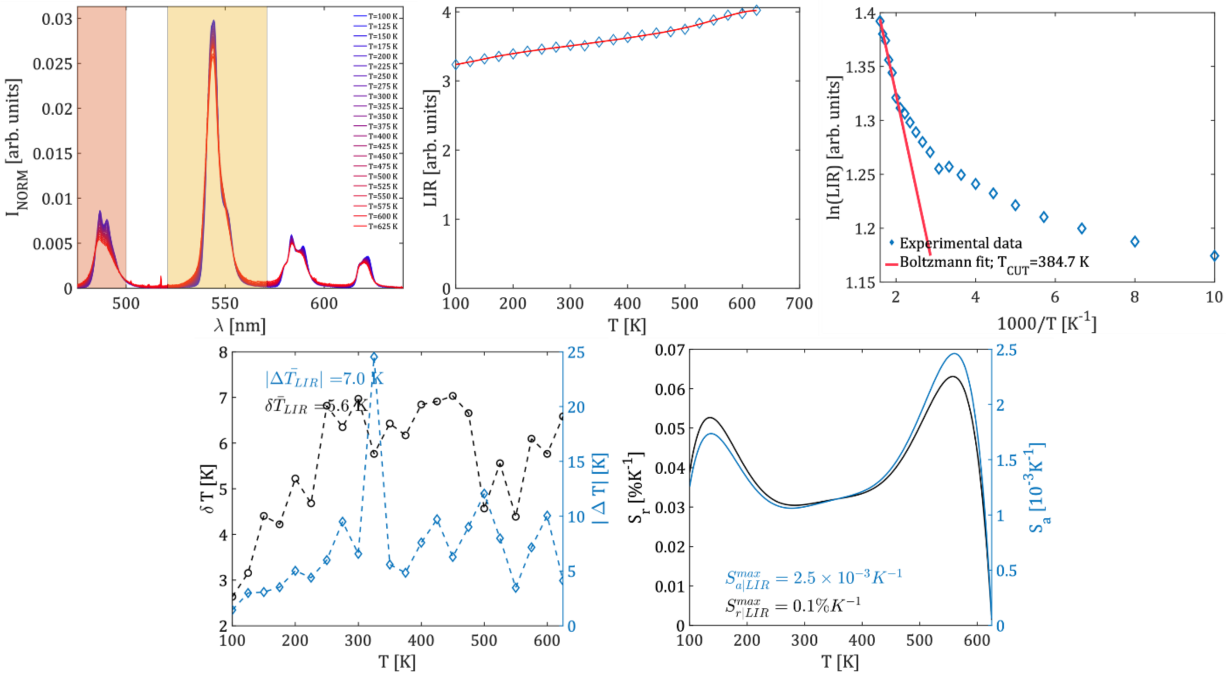

**Figure 2** Luminescence intensity ratio approach

## Principal Component Analysis (PCA) approach

Traditional methods for luminescent thermometry usually depend on a single thermometric parameter derived from specific spectral features or temporal characteristics. Common techniques include luminescence intensity ratio (LIR) measurements, which utilize the temperature-dependent population of thermally coupled energy levels; spectral band shift analysis, which observes temperature-induced changes in emission peak positions; bandwidth measurements, which monitor thermal broadening effects; and lifetime-based methods, which rely on temperature-dependent decay kinetics. Although these traditional approaches have been successful in many applications, they inherently use only a portion of the available spectroscopic information, which may limit their ultimate performance.

During typical luminescent thermometry experiments, large amounts of spectroscopic data are generated, but much of this information remains underused in further analysis. For example, LIR measurements usually focus on intensity relationships between specific spectral regions while ignoring the valuable information in other parts of the spectrum. Similarly, band-shift and bandwidth measurements mainly concentrate on individual spectral line properties, and lifetime measurements either consider integrated intensity across the entire spectrum or focus only on narrow spectral windows. The choice of particular spectral regions for analysis is often guided by physical interpretations and theoretical models, which, although providing useful insights, may not necessarily identify the optimal combination of spectral features for achieving maximum thermometric sensitivity.

Principal Component Analysis (PCA) is a powerful statistical technique for reducing dimensionality and recognizing patterns, increasingly used in spectroscopic data analysis. PCA works by converting a large set of potentially correlated variables into a smaller set of uncorrelated variables called principal components, which account for the most important variance in the dataset. This transformation is done through linear combinations of the original variables, with each principal component aligned along directions of maximum variance in the data space.

In luminescence spectroscopy, PCA provides several key advantages for data analysis and interpretation. The method effectively reduces high-dimensional spectral datasets while maintaining the most meaningful features, allowing detection of subtle spectral differences that might be hidden with traditional analysis methods. Treating photoluminescence emission intensities at each wavelength as an independent variable, PCA can analyze the entire spectral range at once, potentially uncovering the best combinations of spectral features for specific analytical goals.

The performance of the PCA-based thermometric method was systematically assessed, with results compared to conventional LIR analysis applied to the same dataset. To determine the thermographic potential we preprocessed all emission spectra, which involved background removal and normalization, setting the maximum intensity value for each spectrum to 1. For the PCA analysis, the spectra measured at each temperature were treated as a part of the same group. We applied PCA using randomly half of the spectra at each temperature from the entire dataset. This procedure produced numerous principal components, each accompanied by a coefficient vector which we can calculate as a scalar product between a coefficient vector and a spectrum vector. In Figure 3a typical spectrum is presented along with values for PC1, PC2 and PC3 coefficient vectors and their significance. Here it can be seen that almost all the influence weight is in PC1 with 91.3%.

The value of the PC1 can be used as a thermometric parameter the same way luminescence intensity ratio (LIR), band shift, bend width, or lifetime can. Figure 3b shows the mean value of all PC1 at corresponding nominal temperature (red diamonds).

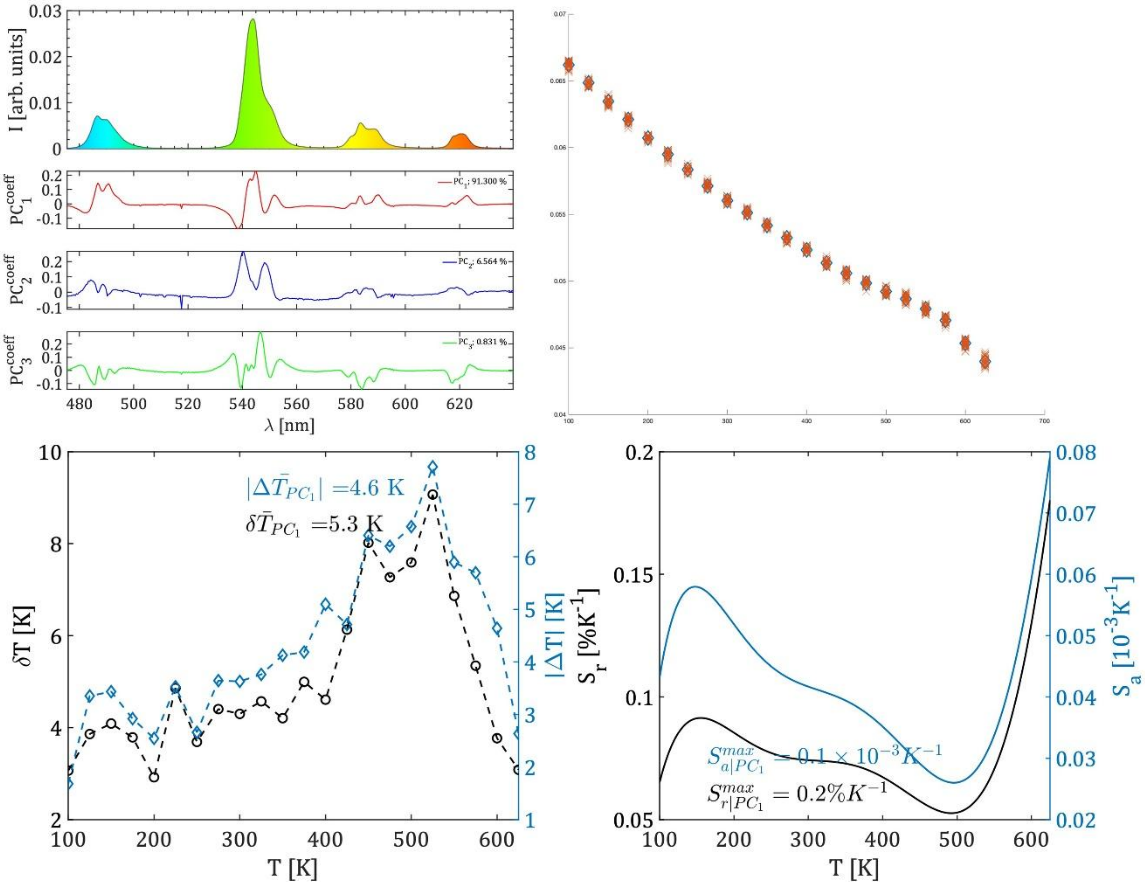

**Figure 3** Principal Component Analysis approach

Based on this, absolute (Sa - blue line) and relative (Sr - black line) sensitivities, average accuracy (ΔT – blue diamonds), precision (δT – black circles) were calculated and presented in Figure 3.

To conclude, all thermographic features performed better when using the PCA approach compared with conventional LIR, even though the same dataset was used as the starting input.