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## Flour moisture detection with an europium-based luminescent sensor

Francisco Fueyo-González<sup>a,#</sup>, Anabel Santiago-Cenit<sup>b</sup>, Rocío Villodres<sup>b</sup>, Ignacio Saiz<sup>b</sup>, Giulia Micolonghi<sup>b</sup>, Eva M. Talavera<sup>b</sup>, Sébastien Teychené<sup>c</sup>, Isaac Rodriguez-Ruiz<sup>c</sup>, Rosario Herranz<sup>a</sup>, Angel Orte<sup>b</sup>, Emilio Garcia-Fernandez<sup>b,\*</sup> Juan A. González-Vera<sup>a,b,\*</sup>

<sup>a</sup>*Instituto de Química Médica (CSIC). Juan de la Cierva 3, 28006 Madrid, Spain.*

<sup>b</sup>*Nanoscopy-UGR Laboratory. Departamento de Fisicoquímica. Unidad de Excelencia de Química Aplicada a Biomedicina y Medioambiente, Facultad de Farmacia, Universidad de Granada. Campus Cartuja, 18071, Granada, Spain. E-mail: [gonzalezvera@ugr.es](mailto:gonzalezvera@ugr.es), [emiliogf@ugr.es](mailto:emiliogf@ugr.es)*

<sup>c</sup>*Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INP, UPS Toulouse, France*

<sup>#</sup>*Current address: Department of Medicine, Translational Transplant Research Center, Immunology Institute, Icahn School of Medicine at Mount Sinai, New York, USA.*

### ABSTRACT

In this work, we describe the application of the self-assembled europium complex **1**:Eu(III) (where **1**: diethyl 8-methoxy-2-oxo-1,2,4,5-tetrahydro-cyclopenta[*de*]quinolin-3-yl)phosphonate) for the analysis of water content of wheat flour as well as from a variety of other food raw materials. The methodology herein described represents a robust and accurate way for the detection of small amounts of water in food, providing comparing results with well-established methods such as thermogravimetry and Karl-Fischer titration. Interestingly, as an advantage over other methods, our luminescent-based approach can be implemented in lab-on-a-chip microfluidic devices for real-time and on-line detection of water content of food samples. Additionally, the remarkably long luminescence lifetime of Eu(III) allows the use of state-of-the-art imaging strategies based on PLIM microscopy for the direct visualization of unique water content maps of flour grains.

*Keywords:* Luminescence, lanthanide, sensor, moisture, microfluidic, PLIM.

## 1. Introduction

Water has an important impact on food quality and storage stability as it interacts with food components, influencing their appearance, structure, physical and chemical properties, and stability. Water content affects the taste, aspect, and lifespan of foods. For example, dry ingredients could undergo alterations in consistency of the end product and excess moisture may cause foodstuffs to agglomerate. Moreover, the rate of microbial growth increases with water content and can result in spoiled food batches, with the subsequent economic loss. Therefore, the analysis of water content is of great importance in food production and industry.<sup>1</sup>

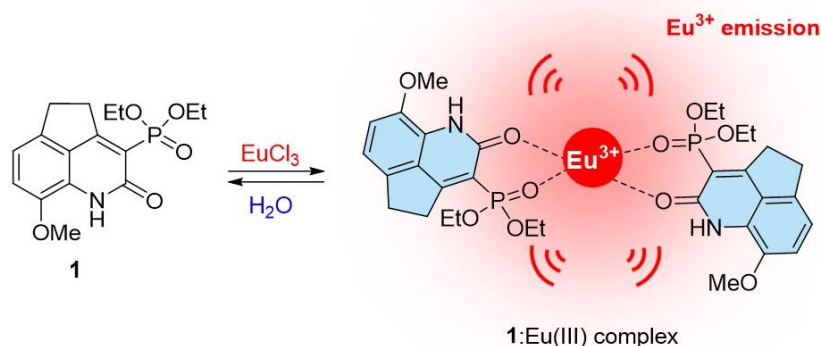
Wheat flour is today one of the most important food raw, dry materials, representing the cheapest source of energy and calories. In fact, bread obtained from wheat flour is one of the main energy and nutrient sources around the world, so the control of its quality is extremely important. For instance, wheat flour must be dry enough to inhibit the growth of molds and other undesirable microorganisms. In this sense, farmers and millers aim for a wheat flour moisture content not higher than 14.5% and, therefore, counting with robust methodologies for wheat flour water content detection is imperative.<sup>2-3</sup> Thermogravimetric methods, which require drying the product at a certain temperature for some time in a drying oven, are currently the standard laboratory technique for water content analysis.<sup>4-7</sup>

However, these methods have problems such as the additional loss of volatile compounds and potential chemical transformations of some of the food components occurring under the analysis conditions. Likewise, strongly bound water may also not be detected at all. Alternatively, a broadly employed and accurate laboratory-based technique to determine water content is the Karl Fischer titration, which consists on the selective reaction of water with a solution of an alcohol, sulfur dioxide (SO<sub>2</sub>) and iodine (I<sub>2</sub>).<sup>8-11</sup> However, this titration method requires costly equipment, and the required chemicals are toxic and expensive. A very sensitive alternative to the Karl Fischer titration is the use of photoluminescent water sensors based on organic molecules or metal–organic hybrid materials. Photoluminescence (PL) measurements present several advantageous features, such as easy preparation,

simple operability, high sensitivity, rapidity, and convenient on-site detection.<sup>12-15</sup> However, one of the main problems when using PL sensors in food samples is the important matrix effect of the samples. Food samples are, on one hand, normally very turbid, due to high content of solids and other sources of light scattering and, on the other hand, these samples may contain potential luminescent interferences. Working in such complex environments requires PL sensors capable of avoiding to a large extent interferences and light scattering. In this sense, PL chemosensors based on the emission of lanthanide ions are of particular interest, due to their high luminous efficiency and narrow spectral widths, and the possibility of applying time-gated PL detection to filter out emissive interferences.<sup>16</sup> Normally, a lanthanide chemosensor requires coordinating the lanthanide ion with suitable organic ligands, including chromophoric groups whose function is transferring energy towards the lanthanide ion (the so-called antenna effect) fostering its emission.<sup>17</sup> Interestingly, the emission from lanthanide ions is very sensitive to quenching by water molecules that can directly interact with the coordination sphere of the metal. This phenomenon has been employed to design specific water sensors.<sup>13</sup> In this field, we have recently reported the discovery of two families of quinolin-2(1*H*)-one derivatives, which can act as selective Eu(III) and Tb(III) antennas, and proposed their use as highly sensitive sensors of H<sub>2</sub>O traces in organic solvents.<sup>18</sup>

Herein we describe the application of the europium antenna diethyl (8-methoxy-2-oxo-1,2,4,5-tetrahydro-cyclopenta[*de*]quinolin-3-yl)phosphonate (**1**, Figure 1), whose europium complex, **1**:Eu(III), showed a limit of detection (LOD) of water in acetonitrile of 0.025 %, <sup>18</sup> to the analysis of water content of wheat flour. The versatility of the newly developed approach was demonstrated through its application to determine the water content of whole white flour, as well as the amount of water of a variety of food raw materials such as diverse nuts (ie: pistachio, cashew, sunflower seed, hazelnut) and honeys of different origin (i.e.: standard honey, lavender honey and rosemary honey). Likewise, we demonstrate the potential use of the sensor in microfluidics lab-on-a-chip devices for on-line determination of water contents of food samples. Moreover, thanks to the exceptionally long PL lifetime of Eu(III), of the order of milliseconds (ms), we have employed PL lifetime imaging microscopy

(PLIM) for the direct visualization of flour grains, which allows the innovative imaging of water content maps.



**Figure 1.** Structure of the Eu(III) antenna **1** and the luminescent self-assembled europium complex **1:Eu(III)** employed as a water sensor to determine the moisture extent of whole white flour, as well as a variety of food raw materials. After the addition of H<sub>2</sub>O, the complex **1:Eu(III)** is quenched leading to a significant decrease in the red, long-lived luminescence emission of Eu(III).

## 2. Results and discussion

### 2.1. Calibration of the sensor

We previously described that the antenna **1** behaves as a self-assembled selective Eu(III) sensitizer in organic solvents, exhibiting the typical red luminescence of this ion upon excitation at 320 nm.<sup>18</sup> Moreover, the addition of H<sub>2</sub>O traces (<2%) to solutions of the **1:Eu(III)** complex in CH<sub>3</sub>CN turned off the characteristic red luminescence of this cation, which set the background to use **1:Eu(III)** as a sensor to determine the water content in organic solvents (Figure 1). Titrations of 54 μM solutions of the **1:Eu(III)** complex (2:1 stoichiometry) in CH<sub>3</sub>CN with increasing amounts of H<sub>2</sub>O (0–2% v/v) were carried out previously, exhibiting a decrease in Eu(III) PL emission with the addition of just 0.005% of H<sub>2</sub>O. The red emission was completely quenched with the addition of 2% of water. The quantitative application of the water sensor to food raw materials required estimating the calibration of the sensor response. The titration results fitted quite well to a linear relationship between  $I/I_0$  and the % of water content (v/v), where  $I$  and  $I_0$  are the PL intensity at 616 nm of the quenched sample solution or the

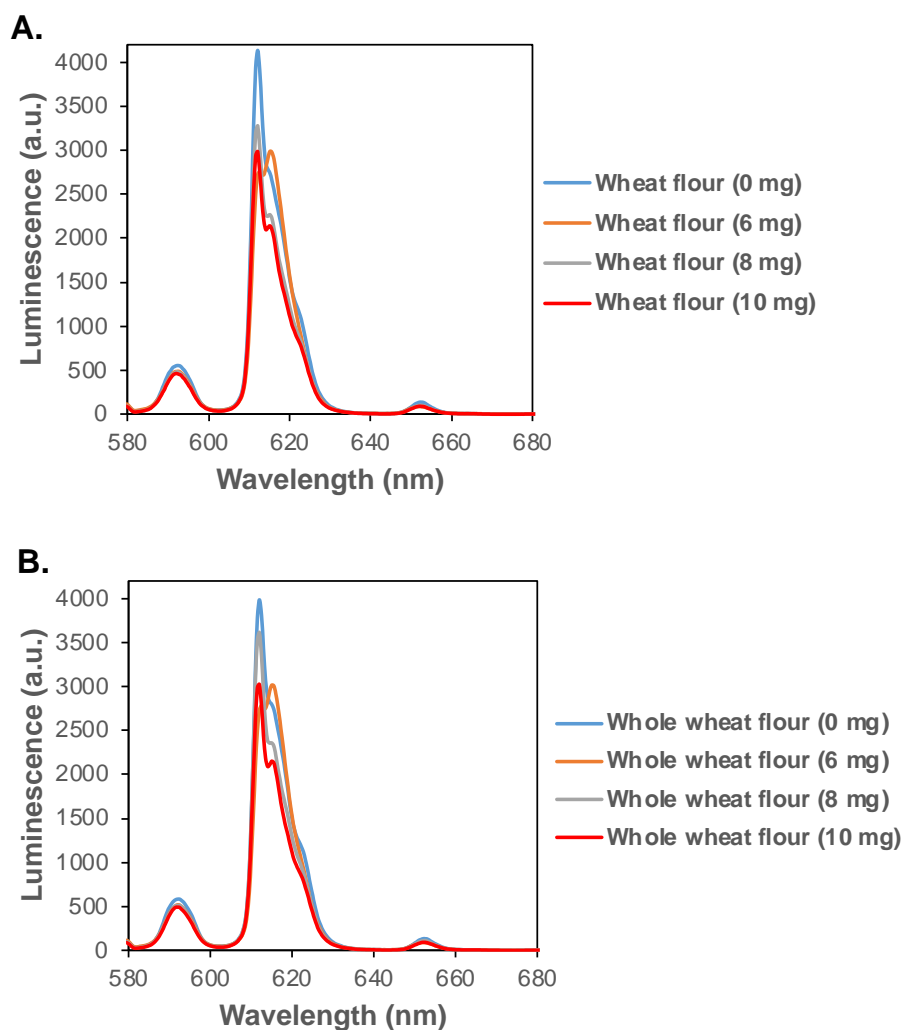
anhydrous blank solution, respectively, following the equation  $I/I_0 = 1 - 8.994 [\%H_2O]$ , which may be used as linear calibration for the determination of water content. This equation allows the interpolation of the relative decrease of intensity of the lanthanide PL emission in a sample of food to extract the water content, considering that the concentration of water extracted from the food in the test solution may be within the calibration range.

## 2.2. *Determination of food water content in wheat flour and other food raw materials*

Since this sensor is capable of detecting extremely low concentration of water and given the importance of wheat flour as a dry food raw material, we selected it to set up a new methodology for water content determination using the europium complex 1:Eu(III) in anhydrous CH<sub>3</sub>CN. Once optimized, the versatility of the new approach was tested by extending the application to different food raw materials of diverse nature. For that purpose, the free water of the raw food, that was previously grinded and/or dispersed conveniently, was extracted using anhydrous CH<sub>3</sub>CN. Subsequently, the mixture of the CH<sub>3</sub>CN food extract and a solution of 1:Eu(III) in dry CH<sub>3</sub>CN resulted in a considerable decrease in PL emission intensity of the metal ion (Figure 2). Then, the subsequent interpolation in the calibration response equation provided the amount of water in the sample and allowed working out the water content in the food.

We first applied our methodology to wheat flour and whole wheat flour, as models of food raw materials. Initially, two critical factors were optimized, i.e., the appropriate dispersion of the food for a correct water extraction in the anhydrous solvent, and the amount of food to maintain the extracted water within the linear range of the calibration curve of the sensor. We analyzed samples of wheat flour and whole wheat flour taking, at least, 5 aliquots of total mass in the 5-15 mg range (Figure S1). As expected, increasing the mass of the aliquot resulted in a larger quenching of the 1:Eu(III) sensor PL emission and shorter  $I/I_0$  ratio values, which correlated well with a larger amount of extracted water. In any case, dividing the amount of water in the extract by the mass of the aliquot resulted in consistent relative water content values in the sample, with final values of  $6 \pm 2\%$  for wheat flour and  $8 \pm 2\%$  for whole wheat flour (Figure 3), which are in very good agreement with the tabulated reference values of

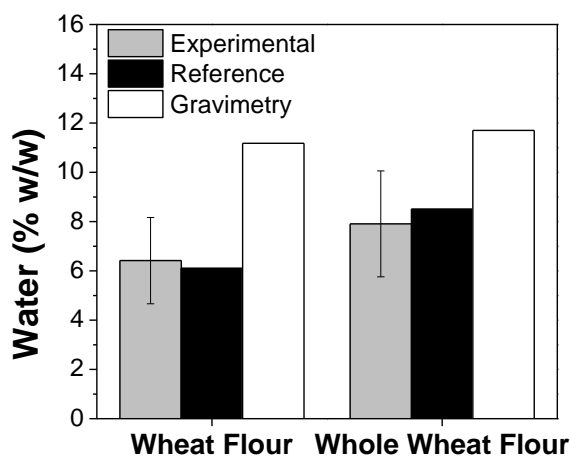
6.1% and 8.5%,<sup>19</sup> respectively, although other sources reported slightly larger values from thermogravimetric analysis.<sup>20</sup>



**Figure 2.** Emission spectra of 1:Eu(III) in the presence of different amounts of (A) wheat flour or (B) whole wheat flour.

Hence, we experimentally compared the results obtained using our luminescent sensor, 1:Eu(III), and the results obtained using the standard thermogravimetry methodology. The thermogravimetric method provided water content values of 11% and 12% for wheat and whole wheat flour, respectively. The results were consistent with reported values using the thermogravimetric approach.<sup>20</sup> This is expected, taking into account that drying techniques measure a mass loss, which is dependent on the chosen conditions, and may arise from other side reactions apart from water

desorption.<sup>21</sup> To this point it is good to take in consideration the different nature of the water content interrogated by each methodology. Whereas, thermogravimetric analysis is able by heating to release moisture and some structural water content, our method focuses on the moisture and free water able to be solvent-extracted. In this sense, the systematic higher content of water by thermogravimetric analysis is consistent.



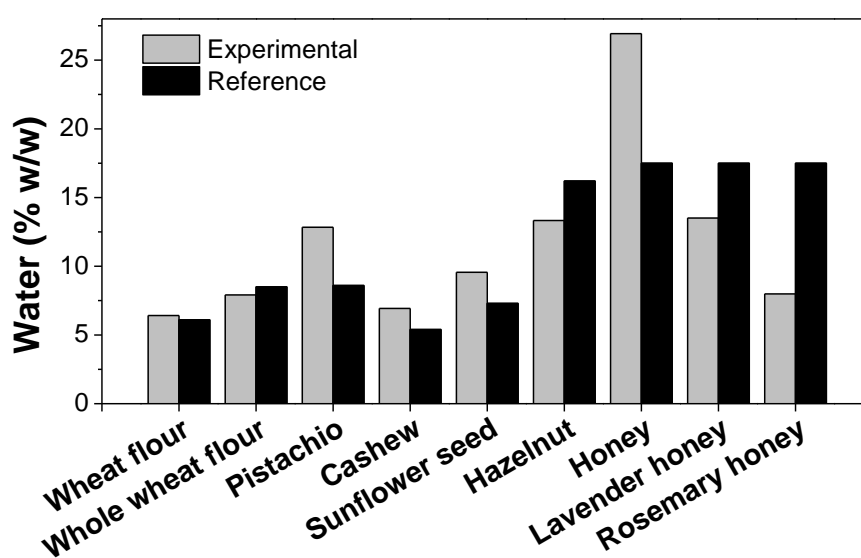
**Figure 3.** Moisture (% w/w) of several food products obtained by luminescence (gray), thermogravimetry (white) and reference value (gray) from <sup>19</sup>.

To test the performance of our methodology to detect variations of water content for a given food, i.e. gain or loss of water, we changed the water content by drying or adding water to wheat flour. The PL emission intensity of the 1:Eu(III) sensor in the CH<sub>3</sub>CN extract was recorded from 5-10 mg of completely dried white wheat flour and 5-10 mg of wet wheat flour (external addition of 10% in mass of water). Additionally, the wet wheat flour was oven-dried at 120 °C for 1 h and kept in a desiccator prior analysis. We termed this sample ‘wet&dried’. As expected, the wet wheat flour resulted in a larger decrease in the PL emission of the 1:Eu(III) sensor than that caused by the other samples. Interpolation in the calibration curve and normalization to the original flour weight yielded the water content values of  $17.4 \pm 1.7$  % for the wet sample and  $8.1 \pm 3.4$  % for the ‘wet&dried’ sample. Interestingly, the ‘wet&dried’ sample recovered after desiccation shows similar water content levels than the original material. This confirms that mild drying, at 120 °C, can be sufficient to remove excess water, loosely adsorbed. For comparison, this drying treatment was also applied to the original raw sample, and we



did not detect significant changes in water content, with an average value of  $7.5 \pm 4.4 \%$ , indicating that this treatment does not have an impact on the strongly bound water layers.

As already shown, we found differences in water content between white wheat flour and whole wheat flour. Then, we extended the application to estimate water content to other food raw materials, such as grainy, nuts, herbal leaves or oil, among others (Figure 4). In most cases, the agreement between our estimations and reference values, obtained via thermogravimetric measurements,<sup>19</sup> was good, except for the results from different types of honey, which exhibited more variability.

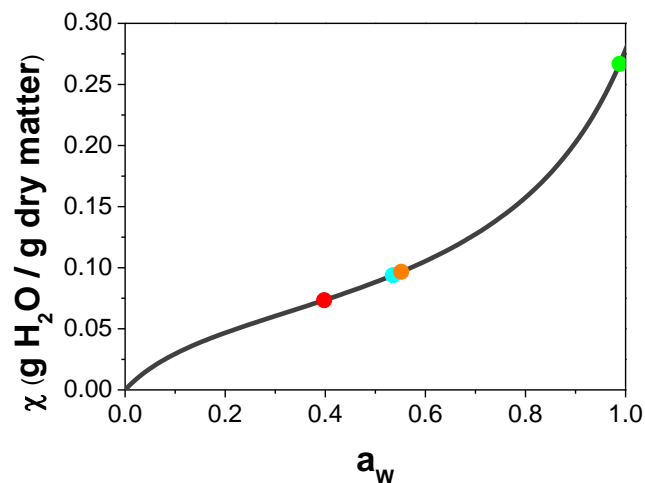


**Figure 4.** Moisture content (%H<sub>2</sub>O, w/w) in diverse food raw materials determined with the europium complex 1:Eu(III) and its comparison with reference values in the literature.<sup>19</sup>

### 2.3. Estimation of water activity ( $a_w$ )

Water activity ( $a_w$ ) is a key parameter in food science to understand the availability of water in food products, allowing us to predict the probability that some degradation reactions of food may take place. The water activity is correlated with the moisture of some food in equilibria with their environment/atmosphere from the well-known isotherm models, such as BET or GAB.<sup>22</sup> For this reason, once the moisture extent of the different food raw materials was determined, next we correlated these moisture values with the corresponding water activity values. For that purpose, wheat flour was

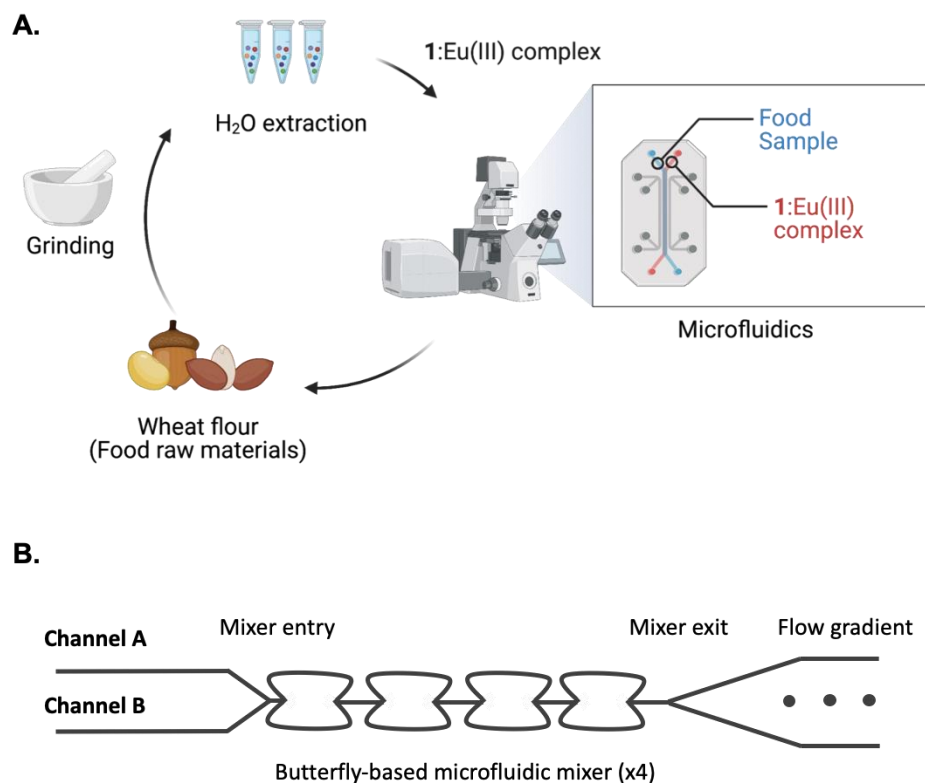
employed as a model, since there are reported several water isotherms for this food.<sup>23-24</sup> Thus, values of moisture content obtained by the previous method (% m/m) were converted into water content per mass of solid food,  $\chi$  (g of H<sub>2</sub>O/g dry solid), in order to associate them to the isotherm reported by Roman-Gutierrez and colleagues.<sup>24</sup> According to the GAB isotherm reported by Roman-Gutierrez and col for wheat flour,<sup>24</sup> we can see three different parts, in which same amount of increase in moisture result in different water activity values, for example an increase of moisture above 0.10-0.15 g of H<sub>2</sub>O/g dry solid results in a significant gain of water activity. This experimental isotherm, fitted to the GAB model, was then employed to extract water activity values from  $\chi$  (Figure 5). We used the calculated water content for the different samples of flour, i.e., wheat flour, wholewheat flour, ‘wet’ wheat sample, and ‘wet&dried’ wheat sample. As shown in Figure 5, we estimated a higher water activity for whole wheat flour (0.53) than for wheat flour (0.40). Moistening the wheat flour with 10% of H<sub>2</sub>O (‘wet’ sample), resulted in a very high water activity (0.99). This result corresponds to the appearance of multilayers of adsorbed water that favors the appearance of microbial growth. Finally, water activity was recovered down to 0.55 when it was desiccated, for the ‘wet&dried’ sample.



**Figure 5.** Water adsorption GAB isotherm (line) for white wheat flour according to Roman-Gutierrez.<sup>24</sup> Points represent the water activity obtained from experimental  $\chi$  values, using the 1:Eu(III) sensor, for wheat flour (red), whole wheat flour (light blue), ‘wet’ wheat flour sample (green), and ‘wet&dried’ wheat flour sample (orange).

#### 2.4. Estimation of water content in a microfluidic chip

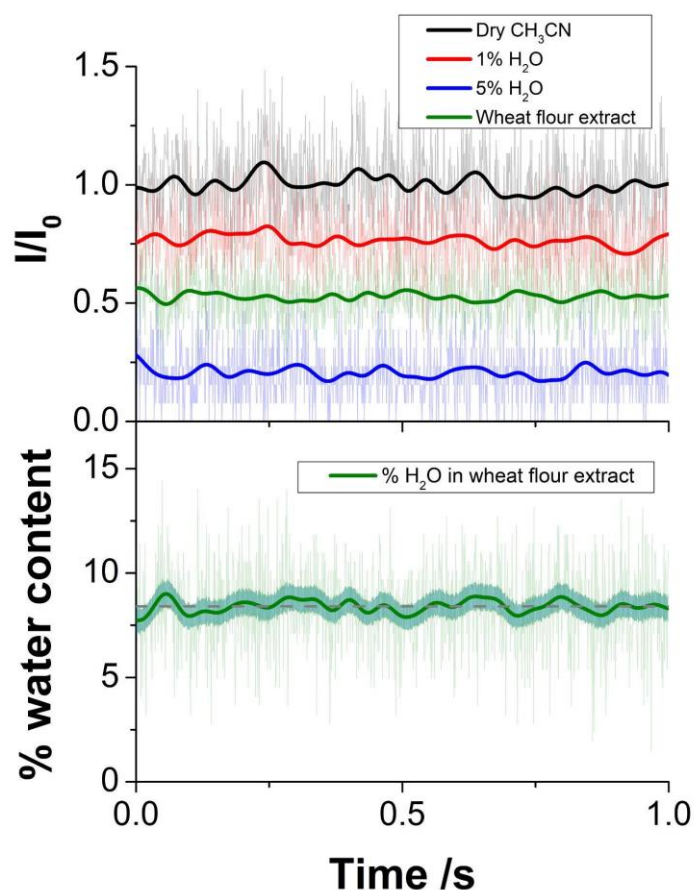
In the food industry, real-time, continuous-flow and *in-situ* analysis of certain analytes is an important tool for rapid and fast quality control, especially when miniaturized. Hence, lab-on-a-chip systems in microfluidic devices have been successfully employed as tools for the detection of a variety of analytes. Therefore, we designed a microfluidic device (see Figure 6 and Figures S2-S5 for details on the design, preparation, characterization and implementation of the mixer chips) to perform real-time continuous-flow water content measurements using the luminescence emission of the 1:Eu(III) sensor. The microfluidic chips were fabricated in OSTEMER by injection molding on a polydimethylsiloxane (PDMS) mold fabricated by a low-cost approach based on standard soft lithography techniques.<sup>25</sup> The microfluidic chip (Figure S3) comprises two inlets for reagent injection, and a butterfly-type passive micromixer allowing for submillisecond mixing times, as reported elsewhere.<sup>26</sup> For our experiments we placed the 1:Eu(III) complex (loaded in anhydrous CH<sub>3</sub>CN; 20 μM of **1** and 20 μM of EuCl<sub>3</sub>) in one of the channels and the other was loaded with either the solvent (anhydrous or non-anhydrous for calibration) or a solvent extraction of raw food materials (Figure 5). The very fast mixing in the chip allowed for real-time measurements of fluctuations in the PL emission of the 1:Eu(III) probe, providing immediate detection of small changes in water content. The micromixer chip was incorporated into a confocal microscope to directly send the excitation light (a pulsed, 375-nm laser) into the channel of the mixer, and collect back the Eu(III) luminescence signal, sent to a point detector with a red-centered bandpass filter (630/60 nm) (see the SI for further details). This setup also allowed us to image the microchannels as diagnostics, confirming the excellent mixing efficiency. The PL emission inside the microchannels showed absence of significant autofluorescence when the testing chamber had no probe and a strong emission when the channel was filled with the europium complex 1:Eu(III).



**Figure 6.** Schematic representation of the (A) microfluidic-based system for the detection of water content in wheat flour and other food raw materials and the (B) employed home-assembled microfluidic chip.

For the use of the micromixer chip for real-time water content measurements, we registered PL emission time traces at different points within the mixing channel to optimize the signal. Figure 7 shows normalized PL time traces ( $I/I_0$ ) from the 1:Eu(III) probe when mixed with anhydrous CH<sub>3</sub>CN, or CH<sub>3</sub>CN spiked with 1% or 5% of H<sub>2</sub>O, clearly showing the quenching of the red emission from 1:Eu(III) caused by water molecules. We calibrated the response of the  $I/I_0$  parameter towards H<sub>2</sub>O content in the microfluidics experiments, given instrumental and experimental differences between the fluorometer and the confocal microscope that prevent using the same calibration equation. For the application with food extracts, the  $I/I_0$  time trace was directly converted into water content traces (considering the dilution factor upon mixing), which illustrate the possibility of real-time determination of water content fluctuations from food extracts (Figure 7). We performed this measurement with CH<sub>3</sub>CN extracts from wheat flour, as explained in the previous section, and obtained an average value of  $8.4 \pm 0.3$  % of water, in good agreement with the results obtained off-line using a cuvette. Remarkably, the implementation

of this system showed its ability to detect real-time and continuous-flow traces of moisture in wheat flour extracts, demonstrating its promising potential in lab-on-a-chip technologies.



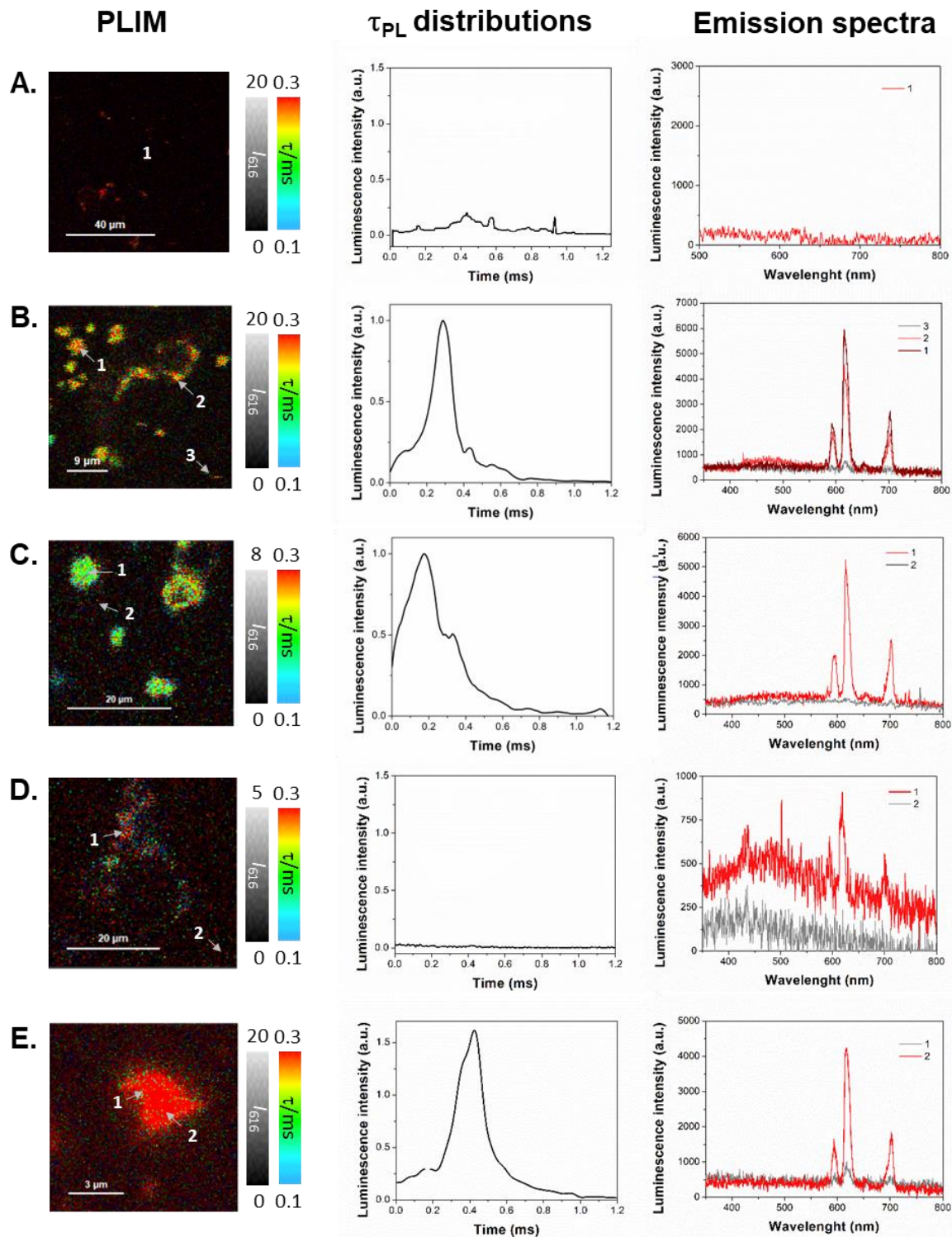
**Figure 7.** A) Normalized intensity traces ( $I/I_0$ ) obtained in the microfluidics device, after fast mixing, for the 1:Eu(III) probe in dry CH<sub>3</sub>CN (black) and containing 1% (red) or 5% (blue) of water, and that in the CH<sub>3</sub>CN extract (3 mL) from 1 mg of wheat flour (green). B) Percentage of water content in 1 mg of CH<sub>3</sub>CN extract from wheat flour measured in real time. Shaded green area represents the standard deviation from the interpolation of the values in the calibration. The average value over the 1 s time trace was  $(8.4 \pm 0.3)\%$  (gray dashed line).

### 2.5. Water content maps in flour grains by PLIM microscopy

Owed to the certainly long PL lifetime,  $\tau_{PL}$ , of the emission of lanthanides ions and, specifically, of the 1:Eu(III) complex ( $0.55 \pm 0.04$  ms in CH<sub>3</sub>CN) and its exquisite sensitivity to quenching by the presence of water molecules, which decreased its  $\tau_{PL}$  from 0.49 to 0.14 ms,<sup>18</sup> we decided to use PL lifetime imaging microscopy (PLIM) to directly visualize grains of flour, of micrometer size (Figure S5). Importantly, this imaging approach allows a time-gated analysis to filter out all potential sources

of natural background fluorescence and scattered light, and therefore increasing the sensitivity, signal-to-noise ratio, and reliability of the detection.<sup>16</sup> The sensitivity of  $\tau_{\text{PL}}$  towards water content allows building up unique water content spatial maps.

Herein, we tested this concept by imaging wheat flour grains, containing different amounts of H<sub>2</sub>O (natural content, 1% or 10% of added water, or dried grains), suspended in anhydrous CH<sub>3</sub>CN with the **1**:Eu(III) probe (20  $\mu\text{M}$  of **1** and 20  $\mu\text{M}$  of EuCl<sub>3</sub>). PLIM images (Figure 8) showed the characteristic Eu(III) PL emission with millisecond lifetime values concentrated in micrometer-sized particles that were attributed to flour grains. This enhanced luminescence on the grain surface arose from adsorbed **1**:Eu(III) complex, as evidenced when compared in controls with and without flour (Figure 8A and Figure S6), and the fact that depending on the confocal plane focused we observed hollow (the confocal plane cut the particle, showing only the outer surface) or full particles (the topmost or bottommost surface of the grain was imaged). For instance, as shown in Figure 8B, PLIM images of wheat flour grains showed strong adsorption of **1**:Eu(III) complex with an average PL lifetime  $\tau_{\text{PL}}$  in the order of 0.31 ms, that was distributed in two lifetime populations, the main at ca. 0.3 ms, and a secondary around 0.5 ms, which suggested that **1**:Eu(III) complex was present in different hydration degrees. The changes in the average  $\tau_{\text{PL}}$  values were followed quantitatively in the lifetime distributions as well as in the overall PL decay traces (Figure S7). To confirm that PL emission was indeed coming from the **1**:Eu(III) complex, we collected the emission spectrum at different points within the flour grains, thanks to the hybridization of a spectrograph to our confocal PLIM microscope (see SI for further details),<sup>27</sup> and found unequivocally the spectral shape of Eu(III), that is narrow emission bands at 593, 616, and 703 nm, correlated with almost total quenching of the antenna **1** emission, as expected for efficient energy transfer towards the lanthanide ion.



**Figure 8.** Representative PLIM images and their  $\tau_{PL}$  distributions acquired in the Eu(III) channel from pixels of the images and emission spectra of selected points collected by irradiating the marked points of samples of A) EuCl<sub>3</sub> and wheat flour; B) 1:Eu(III) complex and wheat flour; C) 1:Eu(III) complex and wheat flour with 1 % of externally added H<sub>2</sub>O; D) 1:Eu(III) complex and wheat flour with 10 % of externally added H<sub>2</sub>O; and E) 1:Eu(III) complex and dried wheat flour.

Interestingly, the addition of 1% of H<sub>2</sub>O to flour grains prior to the suspension in CH<sub>3</sub>CN resulted in a significant decrease in the average  $\tau_{\text{PL}}$  of the complex, from 0.31 to 0.25 ms (Figure 8C), whereas the addition of 10% of H<sub>2</sub>O caused a complete extinction of the complex PL emission (Figure 8D). Interestingly, when we removed the moisture of the wet wheat flour (10% of H<sub>2</sub>O) by oven-drying at 120 °C for 1 h, PL emission of the **1**:Eu(III) complex in the flour grains was restored (Figure 8E), recovering  $\tau_{\text{PL}}$  values around 0.41 ms.

### 3. Conclusions

We demonstrated the quantitative relation of Eu(III) luminescence quenching and water content (%w/w) in CH<sub>3</sub>CN solutions, using our **1**:Eu(III) probe. For very low amounts of water there was a linear relationship between relative luminescence intensity ( $I/I_0$ ) and water content. The sensitivity of **1**:Eu(III) to small amounts of water content in a hydrophobic environment makes it useful for bench applications, to detect small amounts of water extracted from wheat flour as well as from a variety of food raw materials such as diverse nuts (ie: pistachio, cashew, sunflower seed, hazelnut) and honeys of different origin (ie: standard honey, lavender honey and rosemary honey). The methodology herein described represents a robust and accurate way for the detection of water in foods, not based on thermogravimetry which may lead to undesirable reactions, changing the nature and mass of the food. Remarkably, our method can be implemented in lab-on-a-chip microfluidic devices for real-time and on-line detection of water contents in food extracts. Moreover, the exceptionally long PL lifetime of Eu(III) permits the employment of state-of-the-art imaging strategies based on PLIM microscopy for the direct visualization of unique water content maps in micrometer sized flour grains.

#### Conflict of interest

The authors have no conflicts of interest to declare.



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## Supplementary Material

Supplementary material to this article can be found online at

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