Calibration free optical pH sensing using physico-chemical modeling of fluorescein grafted silica fibers

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Abstract:

Dual emission wavelengths fluorescent indicators like SNARF® allow measuring pH by calculating the ratio of the emitted fluorescence at two distinct wavelengths. This ratiometric technique is however not calibration free and molecule manufacturers advise users to perform a pre-calibration using the acidic and basic endpoints of titration respectively.

pH sensing is based on the monitoring of the acid-base reaction which occurs in the indicator layer grafted at the end of an optical fiber. Calibration is required to account for degradation of the sensor probe due to aging or repetitive use and because the pKa of the acid-base reaction cannot be considered constant. pKa variations are due to several factors like temperature and/or ionic strength of the solution to be measured, structure and thickness of the indicator layer at the end of the fiber. Indeed, pKa can differ from almost 2 units between the value in a low concentration solution and the value in a dense layer close to a solid surface which is the case in fiber optic pH sensors. Furthermore, it is extremely difficult to fabricate pH sensitive fibers with a reproducibility high enough to control the pKa of the acid-base reaction in the sensing volume.

In this conference, we show that modeling the fluorescence properties of ratiometric indicators existing in their 2 acidic and basic forms cannot be used to access calibration free pH sensing. We then explain how pH indicators exhibiting more complex prototropic equilibria can be used to compute not only the pH value but also the value of the pKa at the moment when measurements are performed. We present the complete mathematical modeling of the fluorescence properties of fluorescein and we explain how, from any fluorescence spectrum, it is possible to fit the values of both pH and pKa. This is, to the best of our knowledge, the first example of calibration free micro pH sensor.

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