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Intrinsic determination of pH using a barycentre algorithm to characterise fluorescence from an optical fibre sensor

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Abstract Summary

An algorithm to determine the barycentre of the signal received from a fluorescence-based fibre optic sensor probe has been implemented for the intrinsic characterisation of the fluorescence spectra of a pH sensor using coumarin dyes.

Keywords; pH, Intrinsic, Fluorescence, Barycentre, Optical fibre sensor

I. INTRODUCTION

Fibre optic chemical and biosensors have become a well-established technology over the last three decades, although the take-up of sensors for the measurement of chemical parameters lags that for many physical parameters, such as for determining temperature and strain. Among the range of optic fibre chemical sensors that have been developed, pH sensors are prominent because of the importance of *in-situ* and *in-vivo* pH measurements in various areas of activity, be this medical research, scientific research and industrial applications including structural monitoring of cementious materials. A range of commercial pH sensors is available and include indicator strips, pH electrodes, materials that swell as a function of pH and pH optrodes. These clearly vary in many ways: in sophistication of the measurement, in range and precision of the measurement and in being capable of remote measurement and thus their suitability for certain applications will be affected. The glass electrode is the most common type of pH sensor and works for pH in the range 2.5 – 10.5, but is less reliable for highly acid or alkaline measurements. Fibre optic pH optrodes have also been developed and offer an alternative technology; they have the advantage of small size, immunity to electromagnetic interference, capability of remote sensing and do not require a reference electrode for pH measurement. Many different types of probe configuration have been proposed in the literature and, for example, optical fibre sensors incorporating swellable materials [1] have the advantage of being potentially quite stable over time. Optrodes use a suitable interaction of light with pH-sensitive molecules (indicators) which may be achieved using a range of techniques including colorimetric absorbance, fluorescence lifetime or fluorescence intensity, all of which incorporate an optical detector to determine a measurand-sensitive aspect of the received signal and thus link the measurand to a pre-determined calibration. In sensors of this type, effective immobilization of pH indicators is a major concern in their design and optimization.

A number of approaches to creating effective optrodes have been reported in the literature and in the work of the authors. The first immobilization method considered comprises dyes electrostatically deposited in a polymeric thin film through the use of a layer-by-layer electrostatic self-assembly technique [2, 3]. In this case, ionic strength can be an important issue due to the nature of electrostatic interactions and at extreme pH values irreversible damage may occur within the sensitive film. Consequently, sensors of this type are not suitable for sensing at very high or low pH, which are important in a number of applications. A second method involves a group of dyes entrapped or absorbed within a solid structure, which most commonly is a sol-gel matrix [4-6]. This type of pH sensor is usually easy to make but commonly suffers from disadvantages such as leaching of the dye, cracking and inhomogeneity within the material [7, 8], thereby limiting the utility of the probe thus produced. The third method is based on the covalent binding of the indicator to the supporting material or alternatively directly onto the fibre. The preparation of these sensors is, by comparison, comparatively complex and time-consuming, but with the advantage that they prove to be more reliable and durable since the indicators are effectively bonded to the substrate so are therefore less prone to leach out under normal conditions [9] – a major advantage of such a probe.

Most indicators used so far cover the near neutral pH range and, as discussed, this is a key limitation on the wider acceptance of such sensors. If other pH ranges are to be covered, a different range of indicators along with different

immobilization protocols have to be applied. The work reported in this paper is based on the third of the above methodologies, where a probe has been developed where a polymerizable coumarin dye bearing a carboxylic acid group was designed and synthesized, specifically 7-Vinylbezylaminocoumarin-4-carboxylic acid (**7-VBACC**) as the basis of a sensor probe. Details of the pH probe fabrication, sensor response time, reproducibility and photostability have been reported previously [10] by some of the authors.

Building on that previous work, the motivation behind the current investigation is the development of a long-lasting remote pH sensor that is reliable, accurate and intrinsically calibrated (or self-referenced). Absorption based optical techniques are likely to lose their calibration due to leaching of the indicator, variation in the intensity of the excitation source or various other factors which cause a non-pH-related change in detected intensity. This is also true of a fluorescence based sensor when a measurement is taken at a single wavelength; often the fluorescence is referenced to the intensity of the excitation source which eliminates variability due to source fluctuations [10]. By way of contrast it is possible to identify aspects of the fluorescence spectrum that change intrinsically with pH. In this paper we report the intrinsic determination of pH using the measured linear change in the barycentre of fluorescence from the specified coumarin dye across the pH range 1 to 5. This result is compared to that obtained from an alternative method, a peak wavelength determination technique using the same data.

II. METHODOLOGY

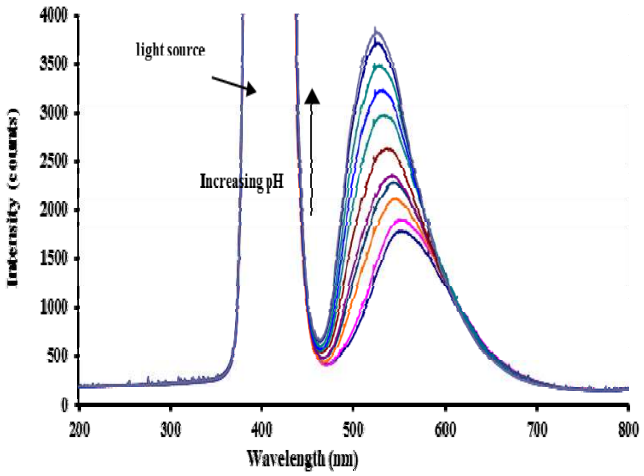

Figure 1. The evolution of the fluorescence spectra of the VBACC probe is shown at various pH in the range from 0.5 to 7. The excitation light source is clearly evident centred near 400 nm[12]

Two common methods of monitoring changes to a measurand using fluorescence are the fluorescence lifetime technique [11] and ratiometric methods. Here the fluorescence is induced by widely available light sources and detected using one, two or a one dimensional array of photodetectors. The fluorescent lifetime method uses the pH dependent change in the decay rate of fluorescence from a material upon removal of the excitation source; the measured lifetime therefore becomes a proxy for pH. A novel approach with this method is to reference the pH sensitive life-time measurement to a pH insensitive phosphor thereby reducing the complexity and expense of the equipment required for the sensor rig [9]. Ratiometric methods which include the fluorescence intensity ratio (FIR) [12] and barycentre techniques can be inexpensive to implement and have significantly reduced susceptibility to the effect of coloration and turbidity of the measured media in comparison with either an absorption or source referenced measurement.

The term “barycentre” is most often used in astronomy to describe the location of the centre-of-mass of a many body system. However, it has also come to be used to describe a weighted mean position of a fluorescence peak, particularly as is the case here where there is a broad spectral feature masking a number of underlying peaks [13-15]. There are different methods that are used to analyse an asymmetric fluorescence intensity spectra and subsequently determine a physical parameter. Characterising fluorescence spectra mainly involves finding the fluorescence maximum; the easiest way is to fit a curve that determines the wavelength corresponding to the maximum intensity. The barycentre method is potentially more accurate as it uses the whole fluorescence spectra. As the observed fluorescence peak wavelength has a marked blue shift with an increase in pH, focusing on finding the barycentric wavelength potentially will improve the measurement accuracy.

Generally practical fluorescence and absorption spectra do not have a predictable traditional shape of a single line that being a Lorentzian, a Gaussian or a combination of both, known as a Voigt distribution. In most of the cases there is more than one peak that overlap rendering peak fitting a rather difficult task and quite inappropriate for a practical device. The barycentre wavelength corresponding to half the area of the intensity fluorescence spectra curve is not always found at the maximum intensity point. For the current consideration the shape of the curve appears to be an exponentially modified Gaussian (positively skewed Gaussian) which is a combination of a symmetric Gaussian component and an exponential component, see Figure 1. The barycentre method [14] is for this application a superior method of uniquely describing a position of the peak as it is independent of the peak widening and any transient intensity fluctuation in the spectra. The barycentre wavelengths for each pH have been calculated using the Origin program and basic linear interpolation techniques. This method gives a description of the change in the average wavelength (centre of mass) of the fluorescence spectra limited to 471.2 nm to 714.2 nm in Figure. 1.

By way of comparison the fluorescence response has also been calibrated using a polynomial fit to the fluorescence data to determine the peak wavelength.

III. EXPERIMENTAL ARRANGEMENT

The experimental arrangement used to measure the response of the pH probe is presented in Figure 2. Light from a light emitting diode emitting at a centre wavelength of 400 nm was coupled through a multimode UV/Visible fibre having a hard polymer cladding, 1000 μm silica core and numerical aperture (NA) of 0.37, using collimation and focusing lenses, into a 2x1 Y fibre coupler, made using two multimode UV/Visible fibres with hard polymer cladding, 600 μm silica core and 0.37 NA, which was connected to the sensor probe with the active sensing region being located at the distal end of the fibre. Following pH interaction with the active region, a portion of the total light emitted from the sensing layer was collected and guided through the other end of the fibre coupler to an Ocean Optics USB2000 spectrometer, the output from which was then displayed on a computer screen. The calibration measurement of the sensor was performed in a 50 mM citrate buffer at different pH (note: citrate does not act as a good buffer at pH higher than 6 and lower than 3; however, citrate was used for all pH to avoid any differences in fluorescence caused by the difference in buffer composition).

The evolution of the fluorescent spectra (Figure.1) obtained, clearly shows a blue shift in peak wavelength and a distinct increase in the fluorescence intensity was observed with increasing pH. More importantly when considering the barycentre technique is the shift to blue wavelengths for the maximum intensity of fluorescence with an increase in pH.

Figure 2. The experimental arrangement used in the evaluation of the probe

The pH variation to the barycentre wavelength (λ_{BC}) is shown in Figure 3. and can be seen to be very linear for pH values between 1 and 5. The sensitivity, S of the measurement was determined to be 1.08% per unit pH change (at a pH of 3) calculated using equation (1) with an uncertainty of ± 0.02%.

In the same figure there is a comparison of the change in peak wavelength of fluorescence as determined using a polynomial fits to the intensity spectra for various pH. The barycentre method appears to be about 10% less sensitive than the peak centre method; however the coefficient of determination is significantly superior resulting a better goodness-of-fit.

(1)

As stated in the introduction the motivation behind the current investigation is the development of a long-lasting remote pH sensor that is reliable, accurate and intrinsically calibrated. The barycentre technique is intrinsic and should be resilient against modest changes in the intensity of the excitation source and to leaching of the indicator. It would rely on a fibre coupled CCD spectrometer integrated with a microprocessor to implement the simple barycentre algorithm to obtain a pH reading. The cost of implementation of the barycentre technique would be higher than that for existing methods, but with an expected improvement in the accuracy of the measurement which is likely to be attractive. The development of practical devices for this method is the subject of ongoing work.

V. CONCLUSIONS

The barycentre method has been demonstrated for the determination of pH using a Coumarin dye-based approach for the indicator across the range 0.5 to 6. The barycentre method is reliable in terms of minimizing the effect of light source fluctuations and indicator leaching, issues seen in practical probes and thus advantageous means of ameliorating these problems when used in practice. Further research is ongoing to develop a simple prototype device that realizes the calculation of barycentre wavelength. On-going investigations will also

focus on the search for other indicators, covering a broader range of pH and which can be configured in practical sensor probes, to which this method can be applied advantageously.

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