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Fibre optic chloride sensor based on fluorescence quenching of an acridinium dye

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ABSTRACT

In this paper, research into the fabrication and characterization of a new fibre optic sensor for chloride ion detection is reported. This sensor is based on the fluorescence quenching of an acridinium dye, which is covalently bound to polymer substrates, in presence of chloride ions. The active material is formed as a powder and packed in a tablet form. Calibration data shows that this fibre optic sensor shows a sensitivity to chloride at concentrations larger than 0.1M.

Keywords: chemical sensor, chloride sensor, fluorescence sensor, acridinium dye.

1. INTRODUCTION

Fibre optic sensors have been widely used for chemical sensing over a period in excess of two decades, using colorimetric or fluorescence-based methods^{1,2}. The interest in developing new and effective designs of such sensors continues, in light of a number of advanced applications. These include both biological and environmental sensing, but in this particular paper, the context of the work is on *in situ* structural monitoring. The ingress of moisture and salts to environmental structures is a particular problem with the wide use of common salt on roads to reduce icing in the winter and the chlorides present can permeate structures and cause considerable degradation. Thus to be able to monitor this effect, in the field, is of particular significance for better structural health monitoring.

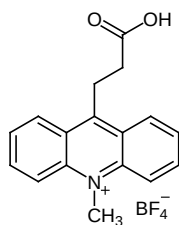
There are a number of techniques available for laboratory monitoring of chloride ions and the commonly used approach is to use the electrochemical method which, however, has the major inconvenience of requiring electrodes to be embedded inside the concrete structures for measurements³. Apart from the installation issues, there are inherent problems associated with these techniques such as electrode failures, low sensitivity and most important ambiguity in the causes of the impedance change. Optical fibre-based sensor systems installed or retro-fitted to civil structures⁴ have been proven to be capable of playing an important role in the health monitoring, including operating at high temperatures and capable of monitoring chlorides in bridges, dams, buildings and other structures. Thus to create an effective fibre optic chloride sensor to measure chloride ion concentration in structural materials would be very attractive compared to its counterparts using alternative technologies, due to the potential for chemically inertness, robustness, immunity from electromagnetic noise and compactness for use outside the laboratory^{5,6}.

2. MOLECULE SYNTHESIS AND FIBRE OPTICAL FABRICATION

A fluorescent sensor for chloride has been developed, based on collisional quenching of an acridinium dye in the presence of chloride ions, following the well-known Stern-Volmer equation:

$$\frac{F_0}{F} = 1 + K_{sv}[Q] \quad (1)$$

where F_0 and F are the fluorescence intensities in the absence and presence of chloride, respectively. K_{sv} is the Stern-Volmer quenching constant and $[Q]$ is the chloride concentration. The details are not reproduced here but, in summary, the synthesis of acridinium dye **A1** bearing a carboxylic acid functional group for immobilization by covalent binding onto a polymer substrate has been achieved, according to a literature preparation published by Urbano *et al.*⁷.



A1

The dye was then covalently bound to a copolymer prepared from 2-hydroxyethyl methacrylate (HEMA), methacrylic acid and ethylene glycol methacrylate in a powder form through an ester linkage formed between the hydroxyl group of HEMA and the carboxylic acid functional group of the dye. The sensing tablet was prepared by holding a layer consisting of 4 mg of polymer particles in between a quartz disc (6 mm dia.) and a nylon membrane (10 μm pores). The layer was kept in place by an O-ring. The resulting material was excited, as discussed below, and in the presence of chloride ions, the fluorescence of the dye is quenched and this quenching of fluorescence is monitored as being proportional to the concentration of chloride.

3. EXPERIMENTAL SET-UP

The set-up used for the measurements undertaken to calibrate the probe is presented in Figure 1, where light from a LED, emitting at 365nm, is coupled through a multimode fibre, using collimation and focusing lenses, into a 2x1 fibre coupler with the sensor material tablet located at the distal end of the fibre. The fluorescence emitted from the material is collected by the other end of the fibre coupler and passed to an Ocean Optics USB2000 spectrometer and then displayed on a computer screen.

The tablet is constantly maintained in an aqueous solution in order to remain wet. The spectrometer is configured to integrate the light collected over a period of 500ms due to the low intensity of the fluorescence signal generated.

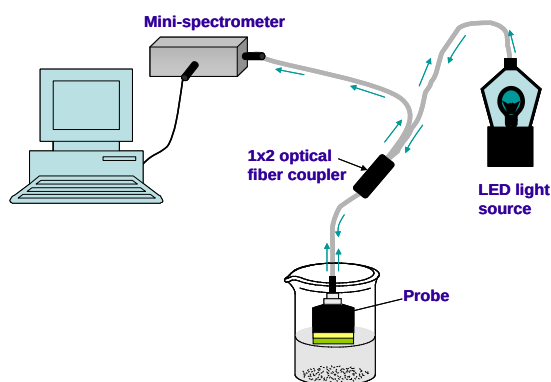


Figure 1: Experimental set-up.

4. RESULTS AND DISCUSSION

The calibration measurements have been performed using five different solutions with the following chloride concentrations: 0M, 0.1M, 0.5M, 1M and 5M. The fluorescence is measured at regular intervals over a period of many minutes (in total up to 240 minutes).

The first study concerns the time evolution of the fluorescence signal. When the tablet is immersed in a chloride solution, it takes some time for the chloride molecule to penetrate the membrane and to interact with the sensing compound. As the fluorescence signal detected is relatively noisy, the average value of the fluorescence signal around the signal peak is required to be determined. Figure 2 presents the time evolution of the fluorescence from the sensor when the tablet is immersed in a high concentration chloride solution (5M). It can be noted that the fluorescence signal begins to stabilize after a period of about two hours. As explained above, this relatively long period is due to the diffusion time required for the chloride ions to penetrate through the membrane and to interact with the sensing acridinium compound. The test was repeated for other concentrations and for a relatively low concentration solution, the sensor signal stabilizes in few minutes as the presence of the chloride ions has a relatively weak influence on the acridinium molecule. For intermediate concentrations, lower than 1M, the fluorescence signal needs about three hours to stabilize as, in this case, sufficient chloride molecules are present in the solution to have an influence on the acridinium molecule. For higher chloride concentrations, the signal stabilization time is around two hours, due to the greater number of chloride ions present in the solution to interact with the acridinium.

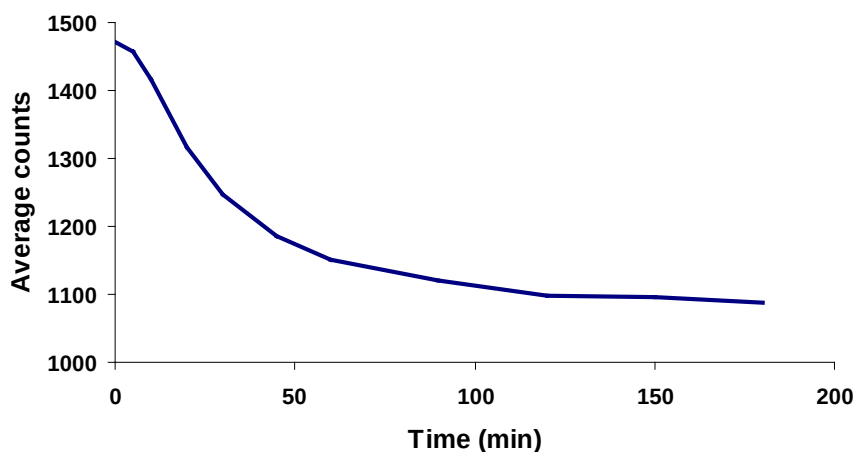


Figure 2: Time stabilization of the chloride sensor when in solution of concentration 5M.

From the time measurement, it is possible to derive calibration data and compare the level of fluorescence of the sensor when immersed in different solutions. Figure 3 shows comparative measured spectra of the tablet sensor for five different concentrations. When the chloride concentration in the solution is below 0.1M, there is no noticeable change compared to deionized (DI) water. Above this threshold, as the concentration increases, fluorescence quenching is observed. The results obtained are comparable to those for the acridinium dye **A1** reported by Urbano *et al.*⁷. A small wavelength shift may be measured, but it is not large or clear enough to be used to estimate, with sufficient accuracy, the concentration of a solution. It may be concluded that this sensor can be used when the concentration of chloride in the solution is above 0.1M and capable of use until at least 5M, the limit of this test. It may be possible to use it for quantitative measurements above this value, but tests have not been made yet to confirm this.

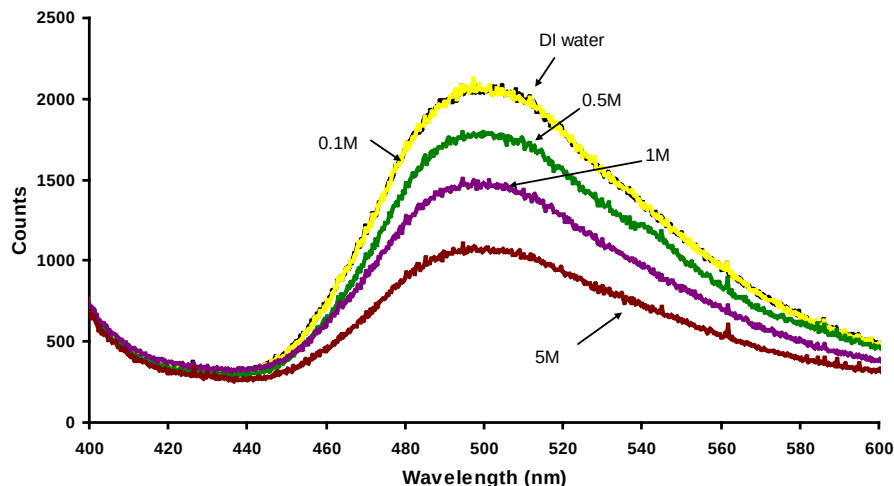


Figure 3: Fluorescence spectra when the tablet is immersed in different solutions.

5. CONCLUSION

In this paper, a new fibre optical chloride sensor design based on fluorescence from an acridinium dye has been reported and results presented on its performance. The fibre sensor thus fabricated has been calibrated using standard chloride solutions of different, known concentrations. The work has shown that in the presence of halide ions, for example chloride, the fluorescence of the acridinium molecule is quenched and the calibration of the sensor probe has shown that the device is sensitive to chloride concentrations larger than 0.1M and has been evaluated for concentrations up to 5M. Research is still on-going to improve the design of the sensing compound and this will allow the detection of lower concentration of chlorides and the sustainability of the compound in high alkaline environment.

6. REFERENCES

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