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Evanescent wave fibre optic sensors for trace analysis of Fe^{3+} in water

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Abstract
In this communication, we discuss the details of fabricating an off-line fibre optic sensor (FOS) based on evanescent wave absorption for detecting trace amounts of Fe^{3+} in water. Two types of FOS are developed; one type uses the unclad portion of a multimode silica fibre as the sensing region whereas the other employs the microbent portion of a multimode plastic fibre as the sensing region. Sensing is performed by measuring the absorption of the evanescent wave in a reagent medium surrounding the sensing region. To evaluate the relative merits of the two types of FOS in Fe^{3+} sensing, a comparative study of the sensors is made, which reveals the superiority of the latter in many respects, such as smaller sensing length, use of a double detection scheme (for detecting both core and cladding modes) and higher sensitivity of cladding mode detection at an intermediate range of concentration along with the added advantage that plastic fibres are inexpensive. A detection limit of 1 ppb is observed in both types of fibre and the range of detection can be as large as 1 ppb–50 ppm. All the measurements are carried out using a LabVIEW set-up.

Keywords: evanescent wave, fibre sensor, iron detection, microbent, pollution monitoring

1. Introduction

The ever-expanding industrialization and concomitant domestic waste generation causes the release of a steadily growing number of pollutants into the environment. Therefore, a great deal of attention must be paid to the pollution of natural freshwater and seawater reserves. Standards for drinking water have evolved over the years as knowledge of the nature and effects of various contaminants has grown. It is considered desirable that drinking water be free of suspended solids and turbidity. In addition, it should be tasteless and odourless, dissolved inorganic solids should be in moderate quantities and toxic substances and pathogens should be absent. With further improvements in water quality standards, additional requirements may be added to this list, making drinking water quality requirements even more stringent.

Use of optical fibre based sensors provides an easy, quick and accurate method to measure the water quality. Over the years, different fibre optic sensors (FOSs) have been developed to monitor various environmental pollutants [1–6]. The most attractive feature of FOSs is that whenever an *in situ* study is necessary, they are able to serve as both the sensing element and the signal transmission medium, allowing the electronic instrumentation to be located remotely from the measurement site. In many places, it is observed that drinking water is not only polluted with various organic materials but also with different metal ions. Iron is known to stain the water supply and it can cause water to appear in red or yellow with a metallic taste. Even though these can be aesthetically

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displeasing, iron is not considered a health risk. In fact, iron in small concentrations is essential to human health. Secondary standards set by the World Health Organization [7] as well as Kerala State Pollution Control Board [8] specify the secondary contaminant level for iron as 0.3 mg l^{-1} (300 ppb). Conventional methods of iron detection are generally based on spectrophotometry and fluorescence quenching [9–11]. In this paper we demonstrate how different types of multimode optical fibre can be modified to act as sensors to detect trace amounts of Fe^{3+} in water. The basic mechanism behind the working of all these sensors is attenuated total internal reflection (ATR) taking place at the sensing region of the fibre. Two types of evanescent wave fibre optic sensor (EWFOS) have been fabricated: one using unclad multimode plastic clad silica (PCS) fibre and another using microbent plastic fibre. The relative merits of the two forms of sensor are compared in terms of the results obtained during the measurements.

2. Theory of operation

EWFOSs generally work on the principle of ATR; i.e. when light propagates through an optical fibre having a lossy cladding, the amplitude of the totally internally reflected wave in the fibre is reduced due to absorption in the cladding region. The optical power transmitted through a multimode optical fibre is distributed in all the propagating modes N, but the fractional power in the cladding for each mode is different. The higher the order M of the mode the larger will be the corresponding penetration depth d_p into the cladding, and hence the larger the fractional power in the cladding [12]. The electric field in the cladding at a distance x from the interface is

$$E(x) = E_0 \exp(-x/d_p) \tag{1}$$

where E_0 is the electric field amplitude of light at the core–cladding interface and

$$d_p = \frac{\lambda}{2\pi(n_1^2 \sin^2\theta - n_2^2)^{1/2}}. \tag{2}$$

Here λ is the operating wavelength, n_1 and n_2 are the refractive indices of the core and cladding respectively and θ is the angle of incidence at the core–cladding interface, each allowed value of which corresponds to a specific mode.

The evanescent wave absorption coefficient γ is proportional to the product of fractional power r in the cladding and bulk absorption coefficient α. But as r is a function of the order of the mode M, the power flow in an optical fibre having an absorbing cladding of length L can be expressed as [13]

$$P(C) = A[\exp(-\gamma_1 CL) + \exp(-\gamma_2 CL) + \exp(-\gamma_3 CL)] \tag{3}$$

where A is a constant and γ_1, γ_2 and γ_3 are three effective evanescent wave absorption coefficients which correspond to different modal groups having different penetration depths and C is the concentration of the absorbing species surrounding the core region. Fortunately, this kind of behaviour makes it possible for the present sensor to act as a logarithmic detector with a large dynamic range.

In the microbent region of a fibre, power coupling occurs between guided modes and leaky modes consisting of both cladding modes and radiation modes, which causes a loss in transmission. The evanescent wave of the cladding modes extends out of the bare fibre which is the basic phenomenon of the working of the present microbent sensor. In a microbent FOS the measurement can be carried out by two detection configurations; one way is to detect power in the core modes, that is known as the bright field detection configuration, and the second approach is to detect power in the cladding modes, known as the dark field detection configuration [14]. It has been shown by Lee *et al* [13] that the basic mechanism by which the power in the core modes and that in the cladding modes is affected in a microbent chemical sensor is evanescent wave absorption in the microbent region.

3. Experimental details

For developing the sensor probe a PCS fibre with core diameter 200 μm and numerical aperture (NA) 0.22 is unclad over a length of 12 cm. This is done by first removing the sheath of the fibre with a sharp razor and then removing the cladding by immersing the unsheathed portion in pure HF for a minute. The bent fibre sensor uses a bare plastic fibre of core diameter 380 μm and NA 0.3. The permanent microbents are written on the plastic fibre by pressing the fibre in between a pair of corrugation plates each having a length of 60 mm and pitch 1 mm [13].

To calibrate the sensor standard solutions of Fe^{3+} are prepared by the thiocyanate method in which Fe^{3+} reacts with thiocyanate to give a series of intensely red-coloured compounds, which remain in true solution [15]. The potassium thiocyanate solution is prepared by dissolving 20 g of AR potassium thiocyanate in 100 ml distilled water. 0.864 g of ferric ammonium sulphate is dissolved in 10 ml concentrated HCl which is further diluted to 1 l. 1 ml of such a solution is equivalent to 0.1 mg of Fe. Knowing this value, test solutions of different concentrations are prepared by again diluting the above solution as required. 40 ml of the test solution is mixed with 5 ml of 2 M potassium thiocyanate solution and 3 ml of 4 M nitric acid, and the resultant solution is diluted to 50 ml. Figure 2 shows the absorption spectra of the solution with various concentrations of Fe^{3+}. It is clearly visible from the plot that the peak absorption of the solution is at 480 nm. The sensitivity of the sensor will be high if the operating wavelength is near this wavelength. This is the motivation for using the 488 nm output of an Ar^+ laser to power the sensor.

A schematic diagram of the experimental set-up is shown in figure 1. The laser radiation at 488 nm from an Ar^+ laser (Spectra Physics, model 171) is coupled to the optical fibre using two mirrors M_1 and M_2 and a microscope objective having an NA of 0.25. The optical fibre is fixed on a pair of X–Y translators, with the unclad/microbent portion of the fibre passing through a glass cell. A laser power meter (Metrologic 545-45) is used to measure the light guided through the fibre, which in turn is connected to a PC using the GPIB (IEEE-488) card of a digital multimeter (HP-34410). Another laser power meter (Newport 1815-C) is used with the microbent fibre to measure the optical power in the cladding modes.

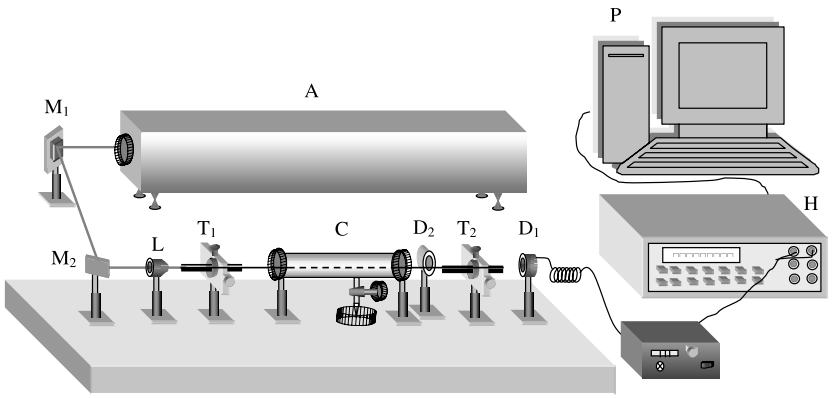

Figure 1. Schematic diagram of the experimental set-up: A—Ar^+ laser, M_1—mirror 1, M_2—mirror 2, L—lens, T_1—X–Y translator, T_2—X–Y translator, C—glass cell, D_1—detector 1 (Metrologic 45-545), D_2—detector 2 (Newport 1815-C), H—multimeter, P—personal computer.

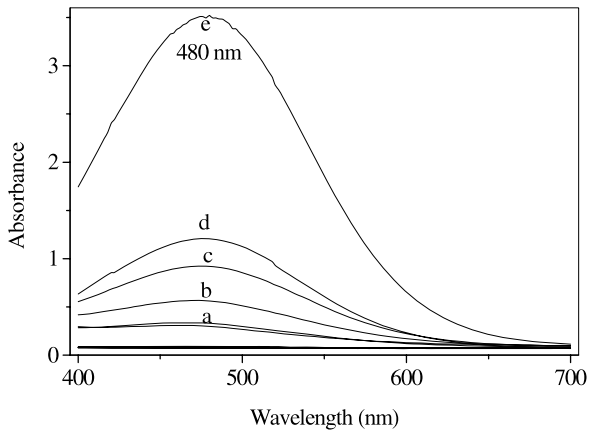

Figure 2. Absorption spectrum of the resulting solution containing various concentrations of Fe^{3+} ($a = 1$ ppm, $b = 2.5$ ppm, $c = 5$ ppm, $d = 10$ ppm and $e = 25$ ppm).

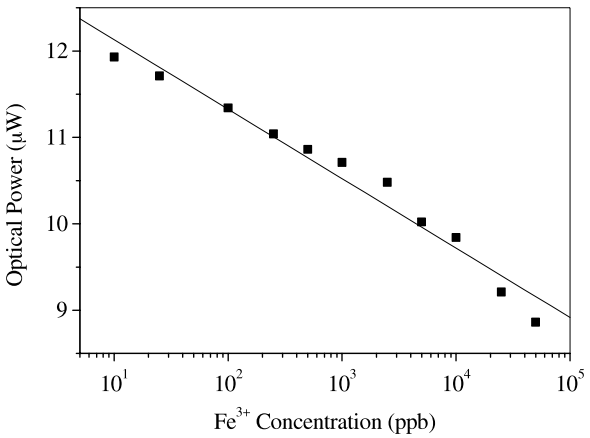

Figure 3. Variation of guided mode power in an unclad multimode PCS fibre with respect to Fe^{3+} concentration.

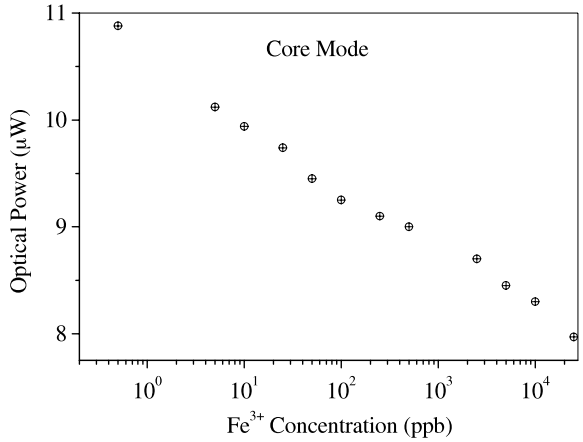

Figure 4. Variation of guided mode power in a microbent plastic fibre with respect to Fe^{3+} concentration.

4. Results and discussion

Figure 3 shows the variation of output power from a 12 cm unclad multimode PCS fibre with various concentrations of Fe^{3+} surrounding the unclad portion. It is evident from the plot that the present device can measure even a few ppb. In addition, the sensor responds in a logarithmic fashion, which makes the device cover a large dynamic range of four to five orders of magnitude, though sacrificing its sensitivity at higher concentrations. This is not the case with conventional spectrophotometric detection where the absorbance varies linearly with concentration. Moreover, it should be noted that with a standard spectrophotometer (Jasco UV-570) the range of detection is limited with minimum detectable concentration as 1 ppm and the maximum as 25 ppm. However, according to the drinking water standards of the World Health Organization and Kerala State Pollution Control Board the permissible limit of iron content in water is 0.3 ppm which is well below the detection limit of the spectrophotometric method.

Figures 4 and 5 show the experimental graphs obtained with a plastic FOS whose sensing region is a 6 cm long microbent portion in the middle of the fibre. Figure 4 corresponds to the change in core mode (guided mode) power with the variation in concentration of Fe^{3+} surrounding the bent portion of a plastic fibre. It is observed that the sensitivity of a 6 cm microbent fibre is almost same as that of a 12 cm unclad PCS fibre. The reduction in the sensing length is obviously an advantage of the former over the unclad fibre sensor.

Figure 5 represents the change in cladding mode power with the change in concentration of Fe^{3+} surrounding the bent portion of the fibre. In contrast to the curve obtained for guided

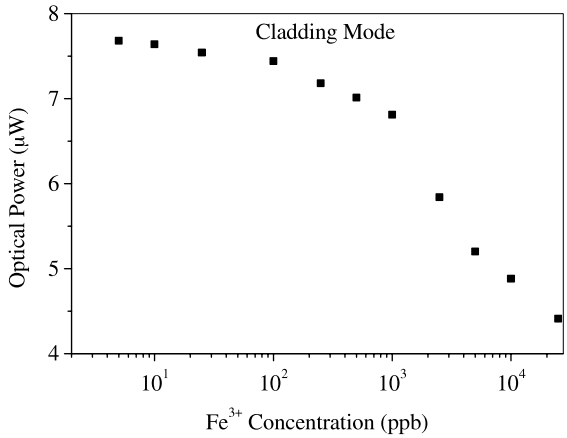

Figure 5. Variation of cladding mode power in a microbent plastic fibre with respect to Fe^{3+} concentration.

modes, the graph in this case is not linear throughout the range of measurements. This is similar to our earlier observation with a generic sensor using a microbent fibre [10]. The non-linearity is mainly attributed to the azimuthal anisotropy in microbending that in turn is restricted to a single plane only. But it should be noted that this configuration of detection of cladding modes is very sensitive above the 1 ppm level of Fe^{3+} concentration.

Comparing the results obtained with the unclad PCS fibre sensor and microbent plastic fibre sensor, the latter is found to be more useful, for the following reasons.

(1) The sensing length can be reduced considerably without any loss of sensitivity,
(2) it is a double detection scheme utilizing both cladding and core modes which enables a cross checking of the readings and hence the reliability of measurements is high,
(3) the sensitivity of detection of cladding mode variation in ppm range is higher than the core mode power variation corresponding to both microbent and unclad fibres and
(4) it uses inexpensive plastic fibre and hence is very cost effective.

It can be seen that both types of sensor are of the intensity modulated type and hence require only a few optical components which will significantly reduce their cost, from the device point of view.

5. Conclusion

In conclusion, we have demonstrated how evanescent wave fields in optical fibres of various types, namely unclad and microbent fibres, can be successfully exploited for detection of trace amounts of Fe^{3+} in water. The results obtained using the two fibres, namely an unclad multimode PCS fibre and a microbent plastic fibre, are used for a comparative study, which reveals that the latter is more versatile in Fe^{3+} sensing application. It can be clearly seen that the sensitivity is only slightly affected by reducing the response time.

Acknowledgments

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References

[1] Radhakrishnan P, Nampoori V P N and Vallabhan C P G 1993 *Opt. Eng.* **32** 62–4
[2] Mizaikoff B 1999 Mid-infrared evanescent wave sensor—a novel approach for subsea monitoring *Meas. Sci. Technol.* **10** 1185–94
[3] Suresh Kumar P, Vallabhan C P G, Nampoori V P N, Sivasankara Pillai V N and Radhakrishnan P 2002 A fibre optic evanescent wave sensor used for the detection of trace nitrites in water *J. Opt. A: Pure Appl. Opt.* **4** 247–50
[4] Leonard K M 1995 Development of a fiber-optic chemical sensor for multicontaminant monitoring of environmental systems *Sensors Actuators* B **24/25** 450–61
[5] Lee S T, Aneeshkumar B, Radhakrishnan P, Vallabhan C P G and Nampoori V P N 2003 A microbent fiber optic pH sensor *Opt. Commun.* **205** 253–6
[6] Lee S T, Jose G, Nampoori V P N, Vallabhan C P G, Unnikrishnan N V and Radhakrishnan P 2001 A sensitive fibre optic pH sensor using multiple sol–gel coatings *J. Opt. A: Pure Appl. Opt.* **3** 355–9
[7] Peavy H S, Rowe D R and Tchobaloglous G 1985 *Environmental Engineering* (New York: McGraw-Hill)
[8] Kerala State Pollution Control Board *Standards and Guidelines*
[9] Esposito B P, Breuer W and Cabantchik Z I 2002 Biometals 2002 *3rd Int. Biometals Symp.* p 729
[10] Olynyk J, Hall P, Sallie R, Reed W, Shilkin K and Mackinnon M 1990 *Hepatology* **12** 26
[11] Lee C 1986 *J. Forensic Sci.* **31** 920
[12] Ruddy V 1990 An effective attenuation coefficient for evanescent wave spectroscopy using multimode fiber *Fiber Integr. Opt.* **9** 142–50
[13] Lee S T, George N A, Sureshkumar P, Radhakrishnan P, Vallabhan C P G and Nampoori V P N 2001 Chemical sensing with microbent optical fiber *Opt. Lett.* **20** 1541–3
[14] Lagakos N, Litovitz T, Macedo P, Mohr R and Meister R 1981 *Appl. Opt.* **20** 167–9
[15] 1978 Determination of iron *Volgel's Textbook of Quantitative Inorganic Analysis* (London: Longman) ch 18, part F pp 738–9