A fibre optic evanescent wave sensor used for the detection of trace nitrites in water

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Abstract
A fibre optic technique for detecting trace amounts of nitrite compounds in water is described. The off-line fibre optic sensor outlined here is based on evanescent field absorption in a test solution formed by the reaction of nitrite compounds in water with suitable chemical reagents. A short unclad portion of a plastic clad silica fibre acts as the sensing region. The experimental results clearly establish the usefulness of the present technique for detecting very low concentrations of the order of 1 ppb (parts per billion) of nitrite compounds with a large dynamic range of 1–1000 ppb. Such a high sensitivity enables the present device to be used for measuring the nitrite content in drinking water.

Keywords: Optical fibre, evanescent wave sensor, pollution monitoring, fibre optic sensor

1. Introduction

Accurate measurement of chemical species in water has acquired great practical significance because of the toxic effects these chemicals can cause to humans. Development of simple, sensitive, low-cost, portable sensors capable of direct measurement of water pollution is of considerable interest in this context. Nitrogen compounds in water present a major health hazard and their accurate estimation is very important in the process of pollution monitoring.

The total nitrogen content of water samples can be present in many chemical forms such as nitrites, nitrates, ammonia etc. When nitrogenous matter is oxidized by the environment, the nitrogen remains mainly in the form of nitrites and nitrates. The presence of appreciable quantities of nitrite can be regarded as an indication of sewage contamination of recent origin. But nitrite is oxidized to nitrate, and consequently a large amount of nitrate points to an earlier sewage contamination [1]. The usual procedure used for the determination of nitrite levels in water is generally based on the formation of a coloured complex species on the addition of specific chemical reagents and by comparison of the intensity of colour thus formed with standards [2]. However, this method has many difficulties such as the need for complex procedures for measuring the chemicals as well as the need for large and delicate instruments. Moreover, these techniques are not sensitive to lower concentrations of the contaminant, especially in the ppb range. Optical fibre technology offers several advantages for chemical sensing over conventional methods and hence it is worthwhile investigating the feasibility of this method to the above problem of nitrite pollution in water. In this paper, we present the details of a simple and sensitive optical fibre sensor, based on evanescent wave absorption, for measuring nitrite concentration in water ranging from 1 to 1000 ppb.

2. The evanescent wave fibre optic sensor (EWFS)

In recent years there has been significant progress in the field of fibre optic sensors for the detection of various chemical species [3–7]. Compared to other sensing methods, the evanescent wave sensing technique offers a number of advantages, especially in chemical sensing applications [8–10]. The interrogating light remains guided in this type of

sensor and no coupling optics is required at the sensing region. Considerable miniaturization can be offered by adopting this technique. Compared to bulk optical methods, EWFSs are highly sensitive and can be used to perform accurate absorption measurements on highly absorbing or scattering media due to a small effective path length. Moreover, since the reagent phase need not be in physical contact with the optical fibre, it is also easy to change the reagent phase. In addition, an EWFS offers significant cost reduction.

3. Theory

Exponentially decaying evanescent fields in the cladding region of the fibre are utilized for developing different types of intensity modulated EWFSs. In this method, evanescent wave absorption in an external medium is obtained by removing a certain region of the cladding of a fibre and allowing interaction of the evanescent field with the absorbing species in the medium. This external medium, which acts as the cladding of the waveguide, absorbs the light at the wavelength being transmitted through the fibre depending on the concentration of the species which absorbs at this wavelength. The power transmitted by an optical fibre with cladding locally replaced by an absorbing medium is given by [8]

$$P = P(0) \exp(-\gamma C L) \tag{1}$$

where P and $P(0)$ are, respectively, the power transmitted through the fibre with and without an absorbing medium over an unclad portion of length L. C is the concentration of the absorbing medium and γ is the evanescent wave absorption coefficient, which is given by

$$\gamma = r_f \alpha_m \tag{2}$$

where r_f is the effective fraction of the total guided power in the sensing region and α_m is the bulk absorption coefficient of the absorbing species. The evanescent wave absorbance is given by

$$A = Ln[P(0)/P]. \tag{3}$$

Substituting (1) and (2) into (3), we get

$$A = r_f \alpha_m C L. \tag{4}$$

For given launching conditions, absorbing materials and the fibre, equation (4) predicts that the evanescent wave absorbance is directly proportional to the species concentration in the unclad region, the effective fraction of the total guided power in the sensing region and the length of the unclad portion of the fibre.

The same reaction, which is commonly used in colourimetric or spectrophotometric methods, is employed in the EWFS for measuring nitrite content in water [2]. In this reaction the nitrite ion, under acidic conditions, causes diazotization of sulphanilamide to occur, and the product is coupled with *N*-(1-naphthyl) ethylenediamine dihydrochloride to produce a violet colouration. The extent of colouration of the resultant solution is directly proportional to the nitrite concentration in water.
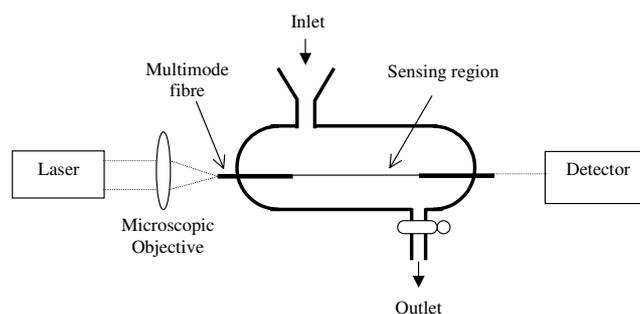
Figure 1. The experimental set-up used for measuring the nitrite concentration in water.

4. Experimental details

In order to exploit the evanescent waves in the multimode fibre, a known length (12 cm) of the cladding of a plastic clad silica (PCS) fibre of 200 μm core diameter (200/380 μm) is chemically removed. A sensor cell of 20 cm length is designed to hold the water samples containing nitrite. It is made of a cylindrical glass tube having a diameter of 4 cm with inlet and outlet provisions. The optical fibre is introduced into the glass tube through the holes provided at the two ends so that the unclad portion of the fibre is within the glass tube and remains straight. The experimental set-up used for the present investigation is shown in figure 1. The output from an intensity stabilized (the maximum drift with respect to mean power level measured over 2 h is $\pm 0.5\%$) green He–Ne laser (JDS Uniphase) emitting at 543.5 nm is coupled to one end of the fibre using a microscope objective having the same numerical aperture. The light emerging from the other end of the fibre is fed to a light detector unit (Digital Power Meter 45-545, Metrologic make) which digitally displays the detected optical power.

Standard water samples having nitrite concentrations ranging from 1 to 1000 ppb are prepared by dissolving sodium nitrite in water. Then sulphanilamide solution is added and after 5 min *N*-(1-naphthyl) ethylenediamine dihydrochloride solution is added to each of the prepared sample solutions such that the ratio between the water samples and the two reagents are 50:1:1, respectively. Now, the colour of the test solution becomes violet and its colour intensity varies with nitrite concentration. These test samples are then allowed to remain for 10 min to complete the reaction, after which the measurements are carried out. When the unclad portion of the fibre is immersed in the test solution, the evanescent field penetrates into the liquid and interacts with it. Since the wavelength of light passing through the fibre is almost close to the peak absorption wavelength of the solution, strong evanescent wave absorption occurs and it increases with the increase in nitrite concentration.

5. Results and discussion

Figure 2 shows the absorption spectra of water samples containing different nitrite concentrations in the wavelength range 400–800 nm recorded using a commercial spectrophotometer (Jasco V–570) set at a spectral bandwidth of 0.1 nm. The absorption peak of the spectra is at around 545 nm and the amount of absorption of light passing through the solution increases with the concentration of the coloured constituent
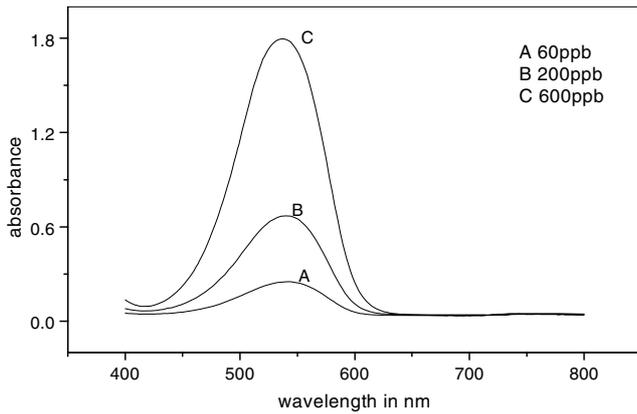
Figure 2. Absorption spectra of water samples containing different nitrite concentrations obtained from the spectrophotometer.
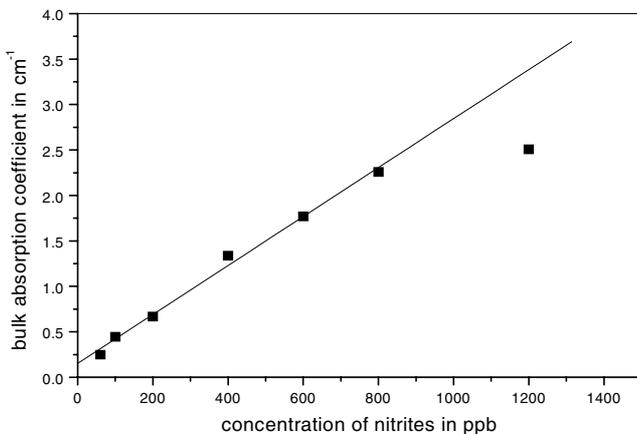
Figure 3. The variation of the bulk absorption coefficient α_m with concentration at the peak absorption wavelength (545 nm) using the spectrophotometric method.

Figure 4. Variation of evanescent wave absorption coefficient γ with concentration using a He–Ne laser emitting at 543.5 nm.
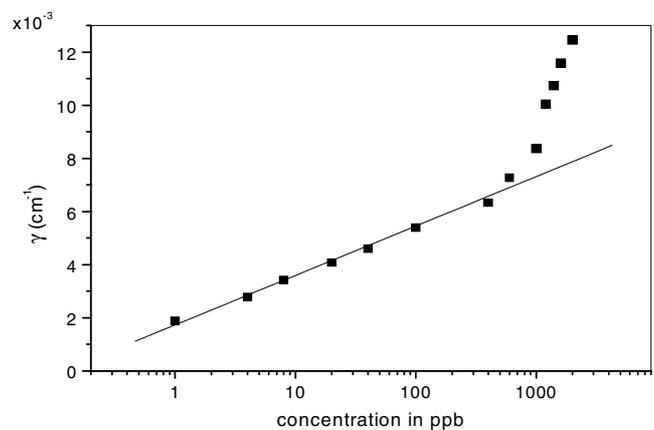
Figure 5. Variation of the evanescent wave absorption coefficient γ with concentration using white light.

in the solution. Figure 3 shows the bulk absorption coefficient α_m of the absorbing species versus nitrite concentrations within the range 60–1200 ppb at the peak absorption wavelength. It is observed that the graph is in accordance with the Beer–Lambert law in the range 60–1200 ppb. However, it should be noted that this method is unable to detect nitrite concentrations below 60 ppb, which can be considered as the threshold detection level for the conventional spectrophotometric method.

In the case of the present EWFS, the experiment is carried out using a He–Ne laser emitting at 543.5 nm, because the resultant solution of the chemical reaction has an absorption peak near to this wavelength. As shown in figure 4, here a good dynamic range from 1 to 1000 ppb of nitrite concentration in water is observed. The observed effect of high sensitivity and wide dynamic range is due to the fact that the amount of light received at the fibre output end is related to the fractional guided power r_f outside the core. r_f varies for different modal groups and hence this causes the sensor to respond in a logarithmic way instead of a perfect Beer–Lambert law fashion [8]. Comparing figures 3 and 4 it is observed that the present system gives a good sensitivity and increased dynamic range in the lower range of concentrations compared to the spectrophotometric method.

Since the evanescent field absorption is the key phenomenon in this set-up, any minor changes to surface

conditions will affect the scale factor of the sensor. In order to avoid this, the sensor cell is carefully cleaned between each sample run. In the present investigation, the trials were performed starting from low concentrations. Moreover, to avoid vulnerability of the exposed silica to surface cracking and other damage phenomena, the removal of cladding is performed carefully with acetone, since it only reacts with plastic and not with silica. Hence we get a smooth clear silica core surface, which is fixed rigidly within the cell.

Figure 5 shows the variation of the evanescent absorption coefficient with concentration using white light as the source instead of a laser. In this case, light from a 50 W tungsten halogen lamp is coupled to one end of the fibre using a short focal length lens. At the other end, the light from the fibre is focused onto a monochromator (McPherson UV 275) with a spectral bandwidth of 0.1 nm, tuned at 543.5 nm and detected using a photo-multiplier tube (Oriel). Here the nature of the graph is the same as that of figure 4, but the dynamic range is considerably limited.

A comparison of figures 4 and 5 reveals that the variation of γ is less when white light is used as the source. It is also observed that the dynamic range of the sensor is reduced to around 600 ppb instead of 1000 ppb when white light is used as the source. This may be due to the fact that the deviation from perfect Beer–Lambert law increases as the bandwidth ($\Delta\lambda$) of the incident beam increases and is particularly severe when $\Delta\lambda$ is greater than the spectral width of the absorption

band of the absorbing species. This results in a sensitivity which falls off with concentration and a consequent reduction in the useful measurement range [10, 11]. To avoid this, the bandwidth of the incident beam should be very narrow, ideally approximating monochromatic radiation, which is justified by the results obtained using the laser source (figure 4). It may be noted that in both cases the absorption increases steeply beyond 1000 ppb, presumably due to the formation of strongly absorbing aggregates and complexes in the solution, which significantly alters the optical properties of the medium [10].

6. Conclusions

We have designed and developed an EWFS for sensitive measurement of trace amounts of nitrite content in water ranging from 1 to 1000 ppb, whereas the conventional methods have been found to be less sensitive at lower concentrations. A comparative study for the detection of nitrites is made using spectrophotometric methods, EWFS powered by a laser source and EWFS with a white light source. Experimental results demonstrate the usefulness of EWFSs in measuring nitrite compounds in water with good sensitivity in the lower concentration range. This establishes that the system can be used for measuring the nitrite content in drinking water and for monitoring the water quality in wells near to fertilizer plants and sewage systems. The cost of the system can be reduced considerably by using a green LED as the source.

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