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Design and development of an LED based fiber optic evanescent wave sensor for simultaneous detection of chromium and nitrite traces in water

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Abstract

The design and development of a cost-effective, simple, sensitive and portable LED based fiber optic evanescent wave sensor for simultaneously detecting trace amounts of chromium and nitrite in water are presented. In order to obtain the desired performance, the middle portions of two multimode plastic clad silica fibers are unclad and are used as the sensing elements in the two arms of the sensor. Each of the sensor arms is sourced by separate super bright green LEDs, which are modulated in a time-sharing manner and a single photo detector is employed for detecting these light signals. The performance and characteristics of this system clearly establish the usefulness of the technique for detecting very low concentrations of the dissolved contaminants.

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1. Introduction

Ground water supplies are increasingly getting affected by the intrusion of toxic chemicals from industrial discharge, agricultural run-off, chemical spills, and leachate from landfills and leaking underground storage tanks. Accurate measurement

of various chemical species in water has acquired great practical significance in the light of the toxic effects these can cause to humans. Chromium is one of the toxic metal ions, a trace amount of which dissolved in water is harmful to humans and other organisms. Chromium based compounds are usually used in tanning industries for the processing of leather and the ground water supplies do get affected by chromium containing discharges from these industries. Consumption of water contaminated with chromium compounds can cause liver and kidney damages. Similarly discharges from

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sewages and fertilizer industries lead to the accumulation of nitrite in water, which get reduced to toxic nitrate by intestinal bacteria causing diseases in human. The nitrites have a greater affinity for haemoglobin than oxygen and thus replace oxygen in the blood complex. Thus the body is denied the essential oxygen and results in a bluish discoloration of the body called ‘blue body syndrome’, and the victim suffocates [1].

According to drinking water standards of World Health Organisation, the maximum limit of chromium allowed in water is 50 ppb and drinking water should be free of nitrites. Detection of these chemicals in water is usually made by atomic absorption spectrophotometry. But this method is not sensitive at lower concentrations of the contaminant, especially in the parts per billion (ppb) range. Optical fibre technology offers several advantages for chemical sensing over conventional methods [2–5] and hence it is worthwhile to investigate the feasibility of this method to tackle the above problem. Different fiber optic sensors (FOS) have been developed to monitor various environmental pollutants [6–11]. In this paper, we present the details of a simple, sensitive and low cost LED sourced optical fibre sensor, based on evanescent wave absorption, for simultaneously measuring chromium and nitrite concentrations in water ranging from 10 to 2000 ppb and from 1 to 1000 ppb, respectively.

2. Theory

The basic mechanism behind evanescent wave fiber optic sensors (EWFS) is attenuated total internal reflection (ATR). Here, the amplitude of the totally internal reflected waves in the fiber is reduced due to evanescent wave absorption in the cladding. Removing a certain region of the cladding of a fiber and allowing interaction of the evanescent field with the absorbing species in the medium can lead to evanescent wave absorption. The external medium, which acts as the cladding of the wave-guide, absorbs the light at the wavelength being transmitted through the fiber and it depends on the concentration of the species. The power transmitted by an optical fiber with clad-

ding locally replaced by an absorbing medium is given by [12]

$$P(L) = P(0) \exp(-\gamma CL), \quad (1)$$

where $P(L)$ and $P(0)$ are, respectively, the power transmitted through the fiber 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

$$\gamma = r_f \alpha_m, \quad (2)$$

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 optical power transmitted through an optical fiber is distributed in different modes and hence r_f is proportional to the number of modes in the fiber. Since the different modal groups have different penetration depths, Eq. (1) can be modified as

$$P(L) = P(0) [\exp(-\gamma_1 CL) + \exp(-\gamma_2 CL) + \exp(-\gamma_3 CL) + \dots], \quad (3)$$

where γ_1 , γ_2 and γ_3 are effective evanescent wave absorption coefficients corresponding to different modal groups. This kind of behavior makes it possible for the present sensor to act as a logarithmic detector with a fairly large dynamic range [13].

3. Experimental details

3.1. Chemicals

All the chemicals used were of analytical reagent grade. The chemicals required for the experiment are sulphanilamide (Sisco Research Laboratories), *N*-(1-naphthyl)ethylenediamine dihydrochloride (Loba Chemie), sodium nitrite (Qualigens Fine Chemicals, Glaxo India), 1,5-diphenyl carbazide (Central Drug House), potassium dichromate (Merck India), sulphuric acid (Merck) and acetone (Merck).

3.2. Preparation of the sensing element

Multimode, plastic clad silica fiber (200/380 μm) is used for making the sensor element. In order to

exploit the evanescent wave phenomenon in the multimode fiber, a known length (12 cm) of the cladding at the middle portion of the fiber is chemically removed and this region acts as the sensing region. To avoid vulnerability of the exposed silica to surface cracking and other damage phenomenon, the removal of cladding is performed carefully with acetone, since it reacts only with plastic and not with silica and hence we get a smooth silica core.

3.3. Sensor cells

Separate and identical sensor cells, each of 15 cm length, are designed for containing the standard water samples of chromium and nitrite, respectively. They are made of cylindrical glass tubes having a diameter of 3 cm with inlet and outlet provisions. Identical sensing elements are introduced into the glass tubes through the holes provided at the sides so that unclad portion of the fiber is within the glass tube and remains straight.

3.4. Electronic components

The super-bright green LEDs are purchased from RS Components, New Delhi and their domes are sword off, the remainder polished prior to use. The light sources are modulated by using a standard 555 timer (NE555). The pin photo detector, 13 DAH 001 is purchased from Melles Griot. The ICs 4016, 4027 and 4017 are from Goldstar and the low noise operational amplifier (LF 356N) and monolithic sample and hold IC (LF398) are from National Semiconductors.

4. Characterization of green LED

The super-bright green LED has a relatively wide emission band of about 80 nm (full width at half maximum) and is centred at approximately 558 nm. This wavelength is well suited for our experiment because the resultant solutions of the chemical reactions between the contaminants (chromium and nitrites) and their corresponding reagents have significant absorption at this wavelength. The output intensity of the LED is about

two orders of magnitude higher than that of commonly used LEDs and is comparable to that of low intensity semiconductor lasers.

5. Design

A schematic block diagram of the instrument is shown in Fig. 1. Identical sensing elements are fixed in the sensor cells in the sensor arms of chromium and nitrite, respectively. The square wave modulated light from two identical super-bright green LEDs emitting at a peak wavelength of 558 nm are coupled to the sensing arms 1 and 2 through the sensing fibers as shown in the figure. The square wave modulator for LEDs is based on a standard NE555 timer, which operates at 2 kHz. Its output is passed through a D-flip flop (CD4027) in order to achieve a perfect 1 kHz signal with 50:50 duty cycle and this signal along with two timing signals are used for generating the modulating signals for the two LEDs. The timing signals Q and \bar{Q} of 100 Hz each with opposite phases are derived from the same 1 kHz signal by using a divide by 10 counter (CD4017). These timing signals and the 1 kHz signal are then fed to the inputs of two AND gates (7408). The two outputs from the AND gates are of same nature but opposite phase, which enable the LEDs to modulate at 1 kHz on a time-sharing basis.

The light signals from the two sensing arms are detected by the PIN photodiode (13 DAH001) and its output is connected to an operational amplifier in the current follower configuration. After sufficient amplification the detected signal is fed to two analog switches (CD4016) along with the synchronising timing signals Q and \bar{Q} from the transmitting side for separating the outputs from the two sensing fibres. Peak value of the signals are obtained from the two peak detectors followed by the sample and hold circuits (LF398). A sampling pulse generator (74121) provides a monoshot sampling pulse of 0.1 ms for the sample and hold circuit. The outputs of the sample and hold circuits are connected to digital multimeters (HP34410) which are interfaced to a computer using the GPIB (IEE488) cards.

Standard water samples having different chromium and nitrite concentrations are prepared by

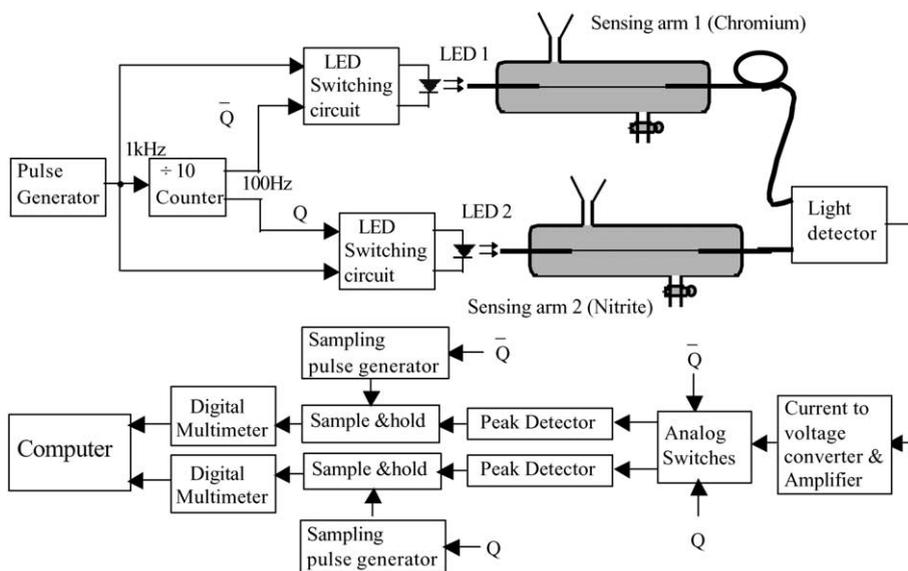


Fig. 1. Schematic diagram of the experimental set-up.

dissolving potassium dichromate and sodium nitrite [14], respectively, in water. The same reactions, which are commonly used in spectrophotometric method, are employed in the present EWFS for measuring chromium and nitrite [14] content in water. When sufficient quantities of 3 M sulphuric acid, 1,5-diphenylcarbazide $[\text{CO}(\text{NH}-\text{NHC}_6\text{H}_5)_2]$ solution and water are added to each of the prepared sample solution of chromium, the color of the test solution becomes violet and the depth of color varies with chromium concentration. Similarly the nitrite ion, under acidic conditions, causes diazotisation of sulphanilamide to occur, and the product is coupled with *N*-(1-naphthyl)ethylenediamine dihydrochloride to produce a violet coloration. The depth of color of this resultant solution is directly proportional to the nitrite concentration in water. When the unclad portions of the fibres are immersed in the test solutions, the evanescent field penetrates into the liquids and interacts with them. Since the wavelength of light passing through the fibre in each of the sensing cell is almost close to the peak absorption wavelength of the resultant solutions, strong evanescent wave absorption occurs and it increases with the increase in concentration of corresponding contaminant.

6. Performance

Fig. 2 shows the absorption spectra of water samples containing chromium and nitrite concentrations with corresponding reagents in the wavelength range 400–700 nm, recorded using a commercial spectrophotometer (Jasco V-570). It can be seen that the peak of the absorption spectrum of the resultant solution formed by the reaction with water samples containing chromium is at around 540 nm and that of nitrite is at around

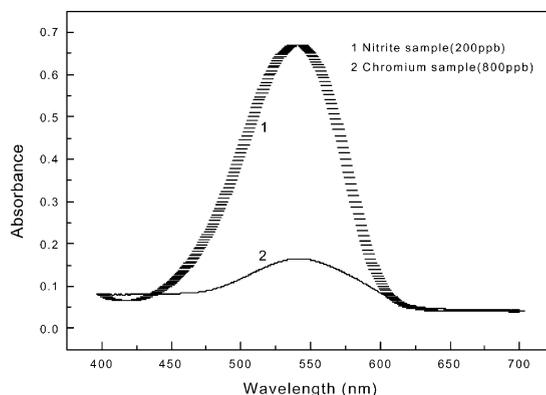


Fig. 2. Absorption spectra of chromium and nitrite samples obtained using a standard spectrophotometer.

545 nm. This is the reason for using green LEDs to power the sensor.

Fig. 3 shows the variation of output voltage with concentration for various concentrations of chromium surrounding the unclad portion of the sensing element in the chromium sensor cell and that of nitrite in the nitrite sensor cell of the device, respectively. The curves clearly show that the present instrument can measure even a fraction of a parts per billion, which is comparable with the existing detection limit of chromium and nitrites. Also the sensors respond in a logarithmic fashion, which enable the device to cover large dynamic ranges. It is worth noting here that a linear variation is observed from 10 to 2000 ppb and from 4 to 1000 ppb, respectively, for chromium and nitrite concentrations in water. But this is not the case with conventional spectrophotometric method, where, the response is in accordance with Beer–Lambert law and hence the absorbance varies only linearly, not logarithmically, with concentration. It is observed that, in the case of chromium and nitrite detection using spectrophotometric method, the lower threshold detection limits are only 200 and 60 ppb, respectively, which are well above the permissible level of the above contaminants in water.

The temporal response of the device to various concentrations of chromium and nitrite are measured by taking the readings continuously in block data collection mode of lab view as shown in Figs. 4 and 5, respectively. It is obvious from the

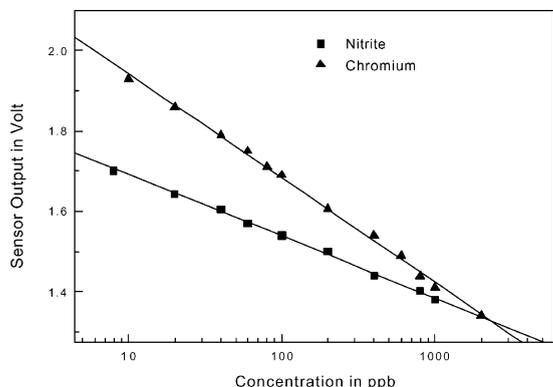


Fig. 3. Variation of output voltage with respect to chromium and nitrite concentrations.

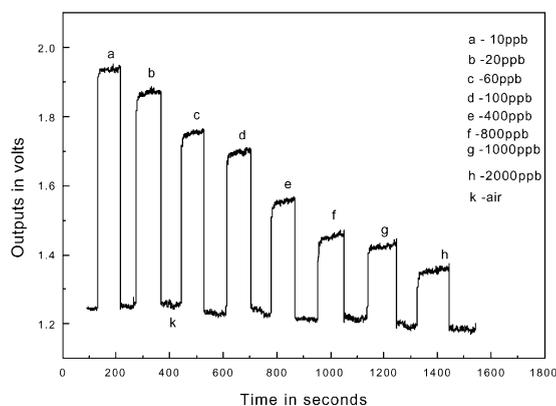


Fig. 4. Response of sensor arm 1 to different concentrations of chromium.

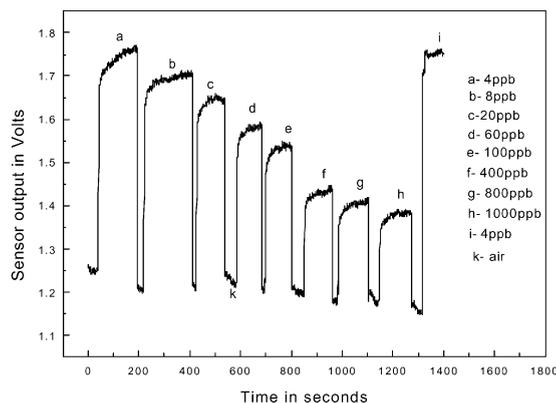


Fig. 5. Response of sensor arm 2 to different concentrations of nitrite.

figures that the signal levels are high and is about 1.97 V for 10 ppb of chromium and 1.78 V for 4 ppb of nitrite.

The valleys in the graphs (k) correspond to the removal of test solutions from the sensor cells, which reveal that the signals have come down almost to the previous valley regions after removing each of the standard test solutions from the sensor arms. This indicates the reversible nature of the sensing elements. In addition, the regions ‘a’ and ‘i’ of Fig. 5 indicate the signal strength corresponding to 4 ppb concentration of nitrite sample, before and after a series of concentration measurements from lower to higher concentrations. It can be seen that the signal strength are almost the same in both

cases. We have also observed the same nature of behavior from sensor arm 1, though it is not indicated in Fig. 4. This reversible nature of the sensing elements eliminates the difficulty of replacing the sensing fibers after each measurement. Since the evanescent field absorption is the key phenomenon in this setup, any minor changes to surface conditions will affect the scale factor of the sensors. In order to avoid this, investigations are performed starting from low concentrations and the sensor cells are carefully cleaned between each sample run.

The response time, the time required for the readings to get stabilized, was also measured for both the sensing arms. To estimate the response times, a separate measurement was carried out, which is not presented here for brevity. For this measurement, the sensor was subjected to only one cycle each of 100 ppb of chromium and nitrite samples in the corresponding arms and the responses are recorded separately on an extended time scale setting. It is observed that the response times are approximately 2 min each for chromium arm and nitrite arm. But 3 s only are required to reach 90% of the stabilized readings.

7. Conclusion

In conclusion, the EWFS developed here can be used for sensitive measurements of trace amounts of chromium and nitrite content in water simultaneously with good dynamic range. This sensor is simple, compact and low cost as the circuitry is based on easily available and inexpensive optoelectronic components. The same device can also be used to measure other contaminants in water by simply replacing the LEDs in accordance with the absorption spectra of the selected species. Moreover, with slight modifications in the LEDs switching side and detector part of the electronic circuits, this device can be used for the simultaneous measurement of many contaminants in water.

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