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Development of fiber optic *p*H meter based on colorimetric principle

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A fiber optic *p*H sensor, having construction of probe based on the colorimetric principle is described. The probe consists of a bundle of fibers with the central fiber as receiving fiber and the outer ring of fibers as transmitting fibers. The LED's of different colours are used as source and photodiode as detector. The probe is tested with *p*H buffer solution prepared by the usual method with universal indicator to get coloured solutions depending upon value of *p*H. The changes in the vicinity of the sensitive tip cause a variation in attenuation of specific reflected visible radiation bands. Initial results and performance specifications using externally added universal indicator are described.

1 Introduction

The *p*H is a number that exactly describes the degree of acidity or basicity of a solution. The *p*H of a solution is important in many different areas such as biochemistry, agriculture, food science, chemical research and engineering, environmental research and pollution control. Protecting our waterways requires constant monitoring of industrial effluent wastewater, as also from washers in mining operation. Chemical plants often have alkaline wastewater. The *p*H measurement is used to guide the proper neutralization of these plants as well as to monitor the final effluent quality.

Electrometric and colorimetric methods are two classical methods for *p*H determination[1]. In the first case the traditional instruments used to measure *p*H of solution, is the glass electrode. The colorimetric method is based on absorption or fluorescence using indicators that reveal the acid or base character of solution through the change of colour. Optical fiber sensors designed to-date are largely based on monitoring the absorption change of several immobilized indicators (bromothymol blue[2], phenol red[3], etc.) or change in fluorescence (e.g. intensity, decay time) of fluorometric indicators (e.g. acridine and 2-napthol[4]). The development of optical fiber based *p*H sensors has been a subject of interest over the years, particularly for biomedical applications[3]. Fiber-optics offers great advantages over conventional potentiometric sensor: possibility of miniaturization, electrical insulation, and immunity from electromagnetic interference. A non-electrical *p*H sensor has attractive features for many biological and medical settings.

In this paper, the development of fiber optic *p*H meter is described. The primary phenomenon used is the detection of change in colour of the solution under test mixed with universal indicator. A compact fiber optic sensor probe capable of illuminating the solution with different coloured light sources (LED's) is developed. The light from emitting fiber passes through solution, gets reflected at the reflector and transverses back through the solution again to get collected by receiving fiber, which guides it to the detector. The responses obtained by the probe from the different standard *p*H solutions are studied. Calibration of the probe is also carried out. The entire system is therefore significantly simpler than most fluorescence-based sensors, as no monochromator or optical filters are employed and both the light source and detector consists only of solid-state electronic components. This paper describes the working principle, construction details, electronic circuits and mechanical assemblies of the *p*H meter. Results obtained are presented and discussed.

2 Measurement Principle

Colorimetry deals with the measurement of coloured intensity. The colour of a substance is due to the absorbance of light waves of certain wavelengths. The absorption of light by solution results in excitation of electrons in its molecule.

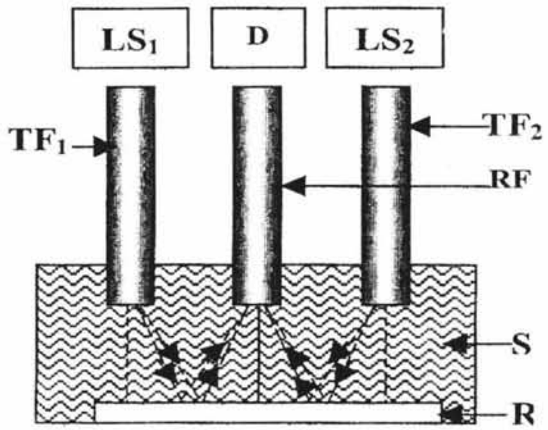

Fig. 1 — Working principle diagram [LS_1 and LS_2: Light Source 1 and 2, RF: receiving fiber, D: detector, TF_1 and TF_2: transmitting fiber 1 and 2, SL: solution, R; reflector]

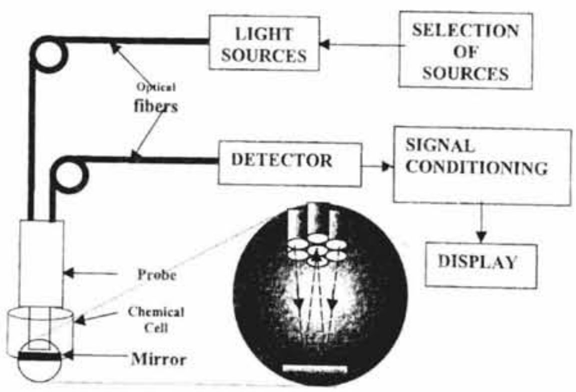

Fig. 2 — Block diagram of experimental set-up for *p*H sensing

The working principle of *p*H meter is illustrated in Fig. 1. The light sources with different colours are adjusted to emit the same intensity. Now when this light travels through the solution from the probe end to reflector and back, depending on the colour absorption characteristics of the solution, different intensities will be received for different colours. These can be plotted against the wavelength of the source to obtain a fairly simple absorption spectrum at those discrete wavelengths. From the spectrum thus obtained for the different *p*H solutions a simplified detection mechanism is developed.

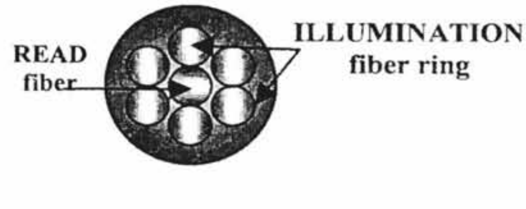

Fig. 3 — Typical fiber bundle arrangement in probe

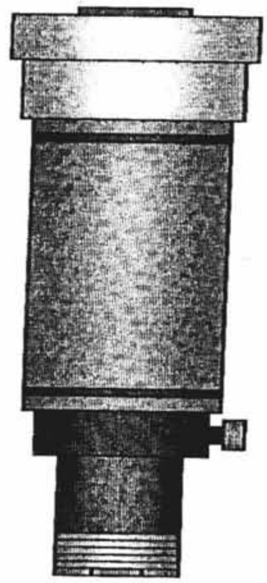

Fig. 4 — Front view of R488-7: Reflection fiber probe

3 Constructional Details of *p*H Meter

Fig. 2 shows the block diagram of fiber optic *p*H sensor based on colorimetric principle. It consists of fiber optic *p*H probe, chemical cell, different light sources with driver circuits, detector, and signal conditioning circuit and display. The designing of fiber optic *p*H sensor probe is a critical job. Various sensing configurations have been reported for chemical sensing[5]. This paper represents the typical fiber arrangement shown in Fig. 3 where the inner fiber collects the return light due to reflection and outer fiber ring transport the incoming light.

Fig. 4 shows front view of designed probe R488-7: Reflection fiber probe. The multi-wavelength reflective probe consists of a bundle of seven fibers – six ILLUMINATION fibers around one READ fiber. Each fiber is a multi-mode plastic fiber of 488 μm core diameter with a numerical aperture of 0.47. The length of each fiber is 90 mm. The fiber tips were polished with zero emery paper. A 30 mm × 6.9 mm brass cylinder houses the fiber bundle. To the sensing tip end of fiber bundle a round cut glass plate is press fitted in order to avoid damage of polished tip due to interaction with chemical under test. A circular brass disc of diameter 24 mm and height 15 mm holds high bright LED's in a circular fashion round a photodiode on one side and the other side holds fibers in front LED's and photodiode. One side of the assembly is enclosed in brass cylinder of 24 mm diameter and 55 mm length, while the other side is enclosed in aluminium cylinder of size 30 mm in diameter and 30 mm in length with DIN connector for electrical connections.

The high brightness 5 mm LED's of different colours are used as light sources. LED's emits relatively narrow wavelength bands. They are also amenable to direct intensity modulation, so that a mechanical chopper is not necessary. The desire to use these devices in design of fluorescent sensors has therefore often been stated in the literature[6]. The laser diodes also can be used in place of LED's, however, because of the requirement of large drive current, required additional heat sinks are considered to be difficult to handle. The driving circuit of LED consists of a *V* to *I* converter, buffers and a subtractor. Photodiode is used as a detector. The signal conditioning consists of buffers, inverting amplifier with variable gain and a subtractor for zero-setting designed with opamps.

4 Experimental Procedure

4.1 Preparation of buffer solutions

A series of solutions of known *p*H between 3.12 and 7.90 are prepared by the procedure discussed below and an equal amount of commercially available universal indicator is added to each of these solutions to get coloured solutions.

The stock solutions of 0.2 M Na_2HPO_4 is prepared by dissolving 28.4 g of Na_2HPO_4 in one liter of distilled water and 0.1M citric acids by dissolving 21.016 g of citric acid in one liter of distilled water. The desired *p*H buffer solution[7] are prepared by adding stock solution in the proportion shown in Table 1.

Table 1 — Proportion of *p*H buffer solution

Sr.No.	0.2M Na_2HPO_4 (ml)	0.1M Citric acid (ml)	Measured *p*H
1	11.40	28.60	3.12
2	16.56	23.44	3.72
3	20.60	19.40	4.40
4	24.18	15.82	5.18
5	29.10	10.90	6.25
6	36.34	3.66	7.31
7	38.90	1.10	7.90

The 0.5 ml of universal indicator (Indikrom, Uaaligens Fine Chemicals) with help of micro-burette is added to each solution and shaken well. The *p*H of solutions is measured with the help of standard *p*H meter of ELICO (India). The intensity of colour of the indicator in an aqueous solution depends upon the degree of dissociation, which is dependent on the *p*H value of the indicator. The solution of lower *p*H values exhibits red colour and those having too high a *p*H value shows an yellow colour. Some solutions having in between *p*H values show an intermediate colour between red and yellow. The absorption of solutions is determined as a function of *p*H at appropriate wavelength.

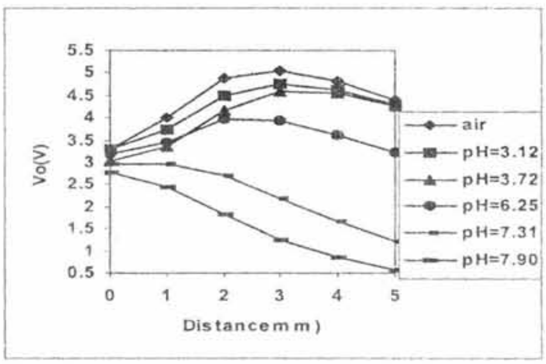

Fig. 5 — Response of sensor with distance variation

4.2 Measurements

Initially the distance between probe and reflector is varied and the output for each distance measured. The results obtained are shown in Fig. 5. It is observed that at the probe-to-reflector spacing of about 2 mm separation between curves corresponding to different values of *p*H is optimum. It was, therefore, decided to carry out all further experiments by keeping the separation fixed at 2 mm.

The experimentation is carried out with the prepared buffer solutions. The fiber optic *p*H probe is dipped into the chemical cell filled with buffer solution of different *p*H values. By using the selection logic, LED of a particular emission colour is selected. As the colour of the solution depends on its *p*H value, and the final reading of voltmeter on the colour of illumination, the reading will in turn depend upon the *p*H value of the solution. Illumination fiber carries the light to the solution. Depending upon the colour of the solution and illumination, light gets absorbed and reflected. The reflected light is detected by the read fiber and gives the corresponding output. The light from the illuminated fiber is reflected at the surface of mirror (reflector) and received by read fiber through the liquid inside the cell. The received output voltage depends upon the *p*H of solution.

5 Results and Discussion

The response of sensor is shown in Fig. 6 in the *p*H range from 3.12 to 7.90. Response thus obtained shows two trends. In the first trend output is low and increases with increase in *p*H value for the light of wavelength < 570 m (green), while in the second trend output is high initially and decrease with increase in *p*H for wavelength > 570 nm.

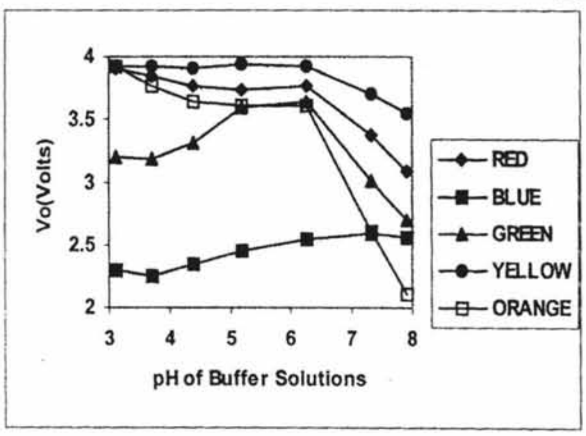

Fig. 6 — *p*H Sensor response

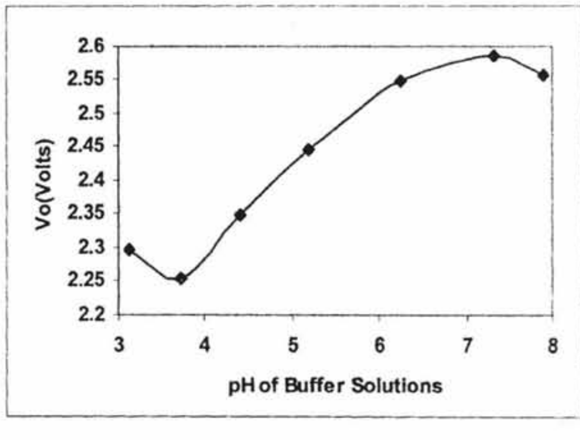

Fig. 7 — Sensor response for blue LED

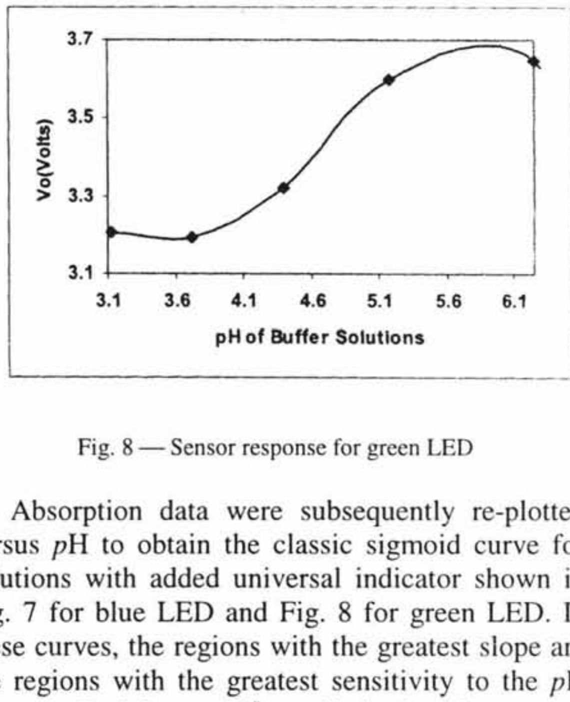

Fig. 8 — Sensor response for green LED

Absorption data were subsequently re-plotted versus *p*H to obtain the classic sigmoid curve for solutions with added universal indicator shown in Fig. 7 for blue LED and Fig. 8 for green LED. In these curves, the regions with the greatest slope are the regions with the greatest sensitivity to the *p*H change. Badni *et al.*[8] studied the fluorescent response of an impregnated sensitive dye-fluorescein isothiocyemate (FITC) using sol-gel method under the condition of varying *p*H using excitation at 488 nm using fluorescent intensity for *p*H range 6-8. The results obtained matches well with results shown in Figs 7 and 8. Note that sensor response is linear or reasonably linear over *p*H range 3.72-6.25 for blue LED and linear over *p*H range 3.6-5.6 for green LED, while the reported linear *p*H range is 7-9 using a fiber optic sensor based on optical absorption using[9] a indicator compound 5-91. Deboux *et al.*[10] reported the linear range of *p*H 3-10 using sensing fiber of 200 μm Plastic Clad Silica (PCS) fiber with cladding removed leaving 30 mm length of bare silica with methylene blue as indicator in capsule in stainless steel windowed with semi-permeable membrane (ion-selective ALPHA 400 dialysis membrane).

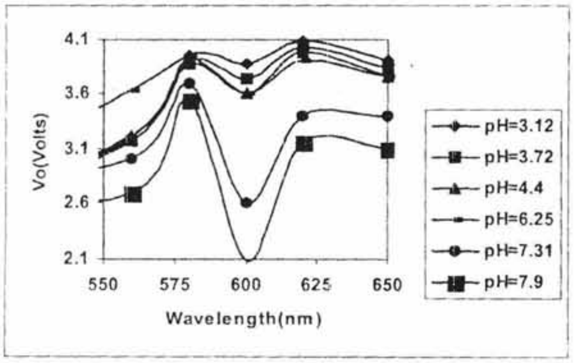

Fig. 9 — Absorption spectrum

The absorption spectra using the developed sensor are shown in Fig. 9. Two distinct peaks are observed at 580 nm and 620 nm with shift in peaks. Results thus obtained are similar to the spectra of phenol red presented by Bacci *et al.*[11], who immobilized the dye on Amberlite XAD-2 polymer beads described by Kirkbright *et al*[2]. There is a clear separation between the magnitudes of peaks for acidic and basic solutions.

The effort described in this paper has lead to the development of fiber optic *p*H meter, which is simple in construction and easy to calibrate and maintain. With the use of commercially available universal indicator it can measure the *p*H in the range of 3.72-6.25 for blue LED source quite reliable. Among the prepared the proposed applications in sugar industries and various agro based products.

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