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Low-Cost Optical Fibre Chemical Sensor for Use in Liquid Acid-Base Titration

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ABSTRAK

Instrumen mudah alih untuk penderia kimia gentian optik telah dibina dalam kajian ini menggunakan diod laser sebagai sumber cahaya dan fotodiod keadaan-pepejal sebagai pengesan. Peranti yang berkos rendah ini menunjukkan rangsangan yang baik dan boleh digunakan dalam tiga jenis titratan asid-bes iaitu i.e. asid kuat – bes kuat, asid kuat – bes lemah dan asid lemah – bes kuat. Hasil kajian yang diperoleh menggunakan instrumen ini, didapati memberikan keputusan yang menyamai keputusan yang diperoleh menggunakan pH meter konvensional.

ABSTRACT

A simple low-cost portable optical fibre chemical sensor instrument has been developed in this study by using a laser diode as a light source and solid-state photodiode as a detector. This inexpensive device is shown to have a good response and can be used in three different liquid acid-base titration studies i.e. strong acid-strong base, strong acid-weak base and weak acid-strong base, by using a suitable pH indicator. The results obtained by using this instrument were found comparable with titration data obtained by using conventional pH meter.

INTRODUCTION

Chemical sensing with optical fibres is one of the most interesting of the emerging sensor techniques. Optical fibre chemical sensors permit the determination of a wide range of anions, cations, gases and organic compounds in solution or gas phases (Narayanaswamy 1985). Impetus to develop these sensors has arisen largely from the need to rapidly acquire data such as chemical compositions of process streams in manufacturing plants, *invivo* body fluids monitoring for clinical purposes and gaseous atmospheres, ground and river waters for pollution monitoring. The basic concept and the advantages of chemical sensors based on optical fibres have been discussed by many authors (Narayanaswamy 1985; Seitz 1984; Alder 1986; Narayanaswamy and Sevilla 1988; Wolfbeis 1986; Morris 1989; Narayanaswamy 1993; Saari 1987).

To date, quite a number of optical fibre chemical sensors for pH measurements have been reported in the literature. The pH indicators for these sensors could be either immobilised on a support (Alabbas *et al.* 1989;

Wolfbeis *et al.* 1992; Munkholm *et al.* 1986; Ding *et al.* 1991; Kirkbright *et al.* 1984; Peterson *et al.* 1980; Moreno *et al.* 1990; Gupta and Marma 1998; Xu *et al.* 1998; Grant and Glass 1997; Pilar *et al.* 1997; Wallace *et al.* 1997; McCullosh and Uttamchandani 1997; Bromberg *et al.* 1996; Zhang *et al.* 1996; Netto *et al.* 1995; Motellier *et al.* 1995, Zhang *et al.* 1995, Ding *et al.* 1991) or directly used in a solution form (Benaim *et al.* 1986; Sahrim *et al.* 1996). Zhu *et al.* (1992) has reported a simple optical fibre pH sensor developed by incorporating a pH paper at the tip of bifurcated fiber. The use of immobilised indicators will require the indicators to be immobilised to a kind of solid support such as entrapment in sol-gel film (Ding *et al.* 1991; Gupta and Sharma 1998; Grant and Glass 1997), a membrane[23] or by simple adsorption on a polymeric support (Alabbas *et al.* 1989; Kirkbright *et al.* 1984; Moreno *et al.* 1990). Without immobilisation, the pH indicator was normally directly added to the solution and the colour changes were monitored by the optical fibre probe. The signal obtained from these sensors, i.e. either reflectance (Alabbas *et al.* 1989; Kirkbright *et al.* 1984; Moreno *et al.* 1990; Benaim *et al.* 1986; Sahrim *et al.* 1996; Christian 1994) or fluorescence[10,1117,20,26] are correlated to changes in pH of the solution.

The use of optical fibre chemical sensor to monitor the progress of acid-base titration has earlier been reported by Shahrim *et al.* (1996), Benaim *et al.* (1986) and Moreno *et al.* (1990) The first two papers have reported using free pH indicators without prior immobilisation i.e. phenolftalien and phenol red, respectively. The work of Benaim *et al.* (1986) was on the development of simple optical pH sensor instrumentation with the probe designed for reflectance measurement. However, the type of acid-base titration carried out with this sensor was not mentioned. Shahrim *et al.* (1996) reported the same type of reflectance probe with a fully computerized instrumentation system for acid-base titration between HCl and NaOH. Moreno *et al.* (1990) has been using cresol red immobilised on the anion-exchange resin as an indicator in acid-base titration between NaOH and strong acids (hydrochloric, perchloric and sulphuric acids), and also weak acids (salicylic, hydrofluoric and phosphoric acids). The instrumentation used in this work was a bulky tungsten-halogen lamp fitted in a spectrophotometer with photomultiplier tube as a detector. The measured parameter was the intensity of the light reflected by the resin, which was guided to the detector by the return fibre.

In this paper we presented a simple low-cost portable instrumentation for optical fibre pH sensor. This sensor can be used to monitor the progress of three different types of acid-base titration by using suitable indicators. Different from the reflectance type of sensors which have been previously developed, the design of the sensor used in this study was based on transmission mode.

METHOD

Chemicals and Solutions

Three different pH indicators are used in this study for titration end-point detection i.e. bromotymol blue (strong acid-strong base titration), bromophenol

blue (strong acid–weak base titration) and tymol blue (weak acid-strong base titration). All the pH indicator solutions were prepared by dissolving 0.050 g of the indicator powder in 20% etanol and the solution was 50.00 mL volume in a volumetric flask.

The acid and base used in this study are hydrochloric acid, HCl; acetic acid, CH_3COOH; sodium hydroxide, NaOH and ammonia, NH_3. The acid and base solutions were prepared through appropriate dilution of the supplied solution to produce acid and base solutions of 0.1 M concentration.

The Electronic Circuits

The complete electronic circuit developed in this study is shown in *Fig. 1.* It consists of a signal generator, a light source, a photodiode, a pre-amplifier, a sample-hold circuit, an amplifier and a display unit. The light from a laser diode will be transmitted to the optical fibre and will be guided by the feed fibre to the detection area where the light will be modulated. The modulated light will be guided by the return fibre to the photodiode. Upon detection, photodiode will produce a small electrical current which will be amplified and transferred to voltage by pre-amplifier circuit. The signal will later be passed to the sample-hold circuit which will produce outputs which are proportional to the signals received by the photodiode when the laser diode is on or off. In such a sequence, an interferent from ambient light will be avoided and as a result, the overall output is only a detected laser diode light intensity which has been modulated at detection area. Output from the sample-hold circuit will later go to the amplifier for further signal amplification before being displayed.

Signal generator circuit: The signal generator circuit developed in this study consists of a multivibrator and a driver (*Fig. 2*). The multivibrator device consists of transistor (TR2 and TR3), timing component, resistor (R6 and R7) and capacitor (C3 and C4). Transistor TR1 and TR4 functioned as a driver for laser diode and sample-hold circuit.

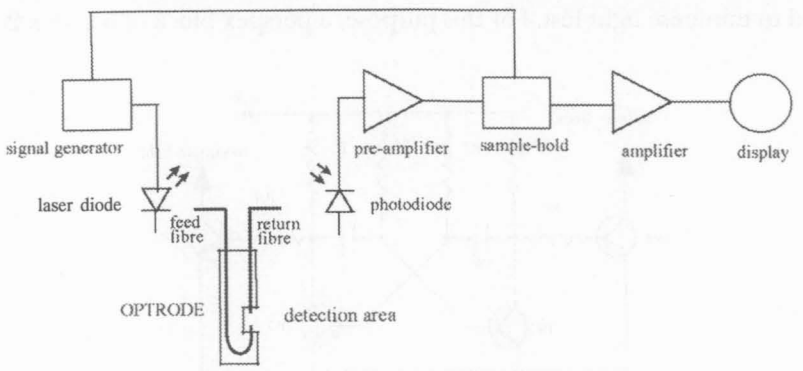


Fig. 1: Electronic circuit for low-cost portable instrument optical fibre chemical sensor

Pre-amplifier circuit: The pre-amplifier circuit used in this study was BIFET operational-amplifier (op-amp) because its input impedance which is high, is suitable for handling small electrical signals. The small electrical current produced by photodiode will flow to the inverting input (-) and then directly to a feedback resistor R_f which will transform the current to output voltage as shown in *Fig. 3 (A)*.

Sample-hold circuit: The components used to build this circuit consist of a diode, capacitor C2 and BIFET op-amp as shown in *Fig. 3 (B)*. An electrical signal in the form of voltage pulse will be filtered and will charge the capacitor C2. When the laser diode is off, the transistor collector TR1 and diode anode will be at zero level and therefore, no signal will pass the diode. Therefore, only a signal pulse is allowed to pass this circuit. The charge at the capacitor C2 will be discharged only through resistor R2 because the input impedance at the op-amp non-inverting input (+) is very high. The discharge duration is governed by the values of resistor R1 and capacitor C2 used. In this study, the discharge time is 1 second.

Amplifier circuit: The output signal produced by the sample-hold circuit is not big enough to be displayed and an amplifier circuit is needed for further amplification of the signal. The amplifier circuit consists of bipolar op-amp as shown in *Fig. 3 (C)*. The values of R_f and R_i used in this circuit will determine the amplification values, E_i. The end of R_i was connected to V_R which, having potential difference of (+) and (-), ensures that the Vo values could be adjusted.

Construction of Optical Electrode (Optrode)

The optical fibre used for optrode construction is of multimode silica type with core diameter of 1 mm and numerical aperture, NA of 0.47. Before using the optical fibre, its surface was polished by using lapping sheets to produce a smooth and flat surface.

The design of the optrode used in this study is shown in *Fig. 4*. A mould made from plasticine was used to incorporate the optical fibre in the resin epoxy. The end of both the feed and return fibres in the detection has to be aligned to minimise light lost. For this purpose, a perspex block of 5 x 18 x 20 mm

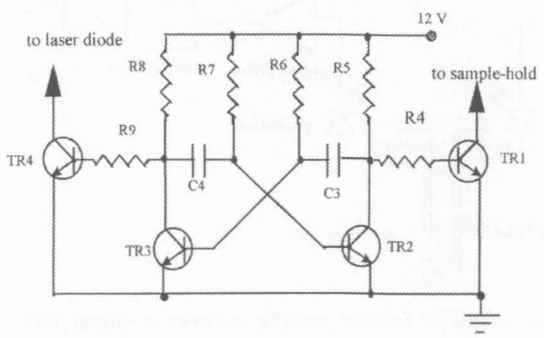


Fig. 2: Electronic circuit for signal generator

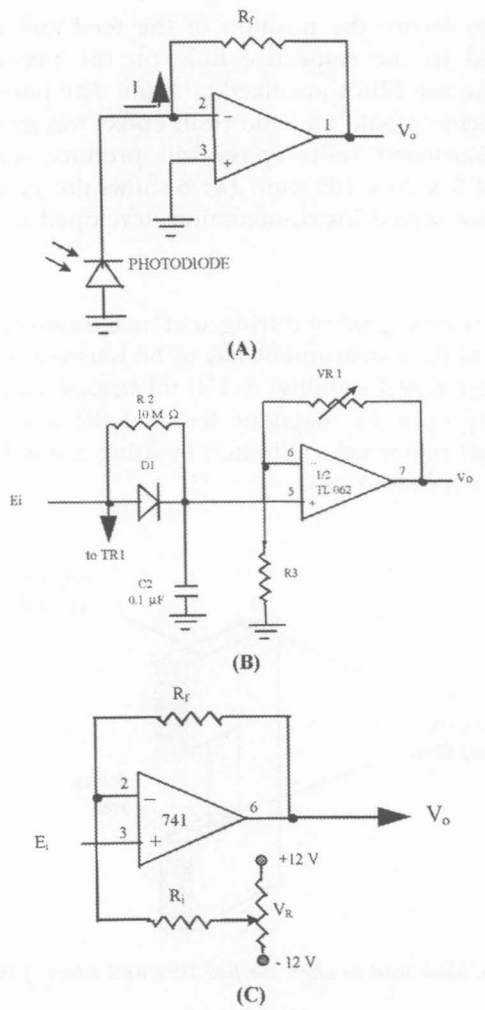


Fig. 3: Electronic circuit for pre-amplifier (A), sample-hold (B) and amplifier (C)

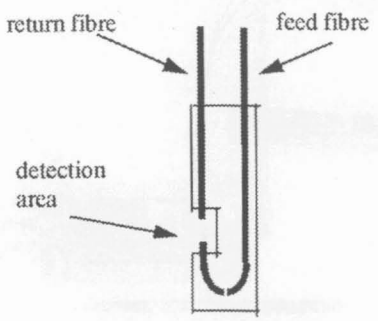


Fig. 4: The design of the optical fibre optrode

(*Fig. 5*) was used to secure the position of the feed and return fibres. Both fibres were inserted in the respective hole on the perspex block and the distance between the two fibres was fixed at 1mm. The perspex block was later placed in the plasticine mould and the resin epoxy was gradually poured into the mould. The hardened resin epoxy will produce an optrode with an approximate size of 5 x 20 x 100 mm. *Fig. 6* shows the picture of the low-cost portable optical fibre sensor instrumentation developed in this study.

Procedures

The instrumentation arrangement during acid-base titration process is as shown in *Fig. 7*. The optical fibre instrument has to be warmed up for about 15 min before use for better signal stability. A 150 ml beaker was used as a titration container where the optrode, magnetic bar and the conventional pH meter were placed. The pH meter was calibrated by using a standard buffer solution of pH 4.0 and pH 9.0 before use.

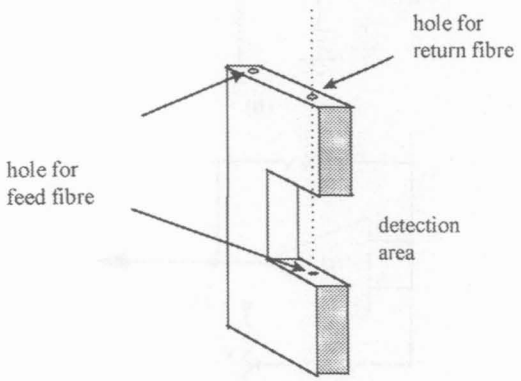


Fig. 5: A perspex block used to align the feed fibre and return fibre in the optrode

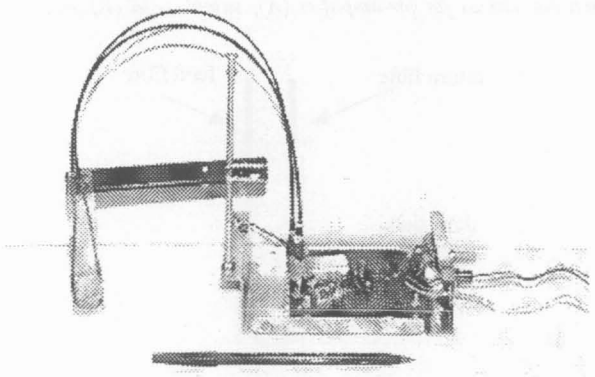


Fig. 6: Instrumentation for portable optical fibre chemical sensor

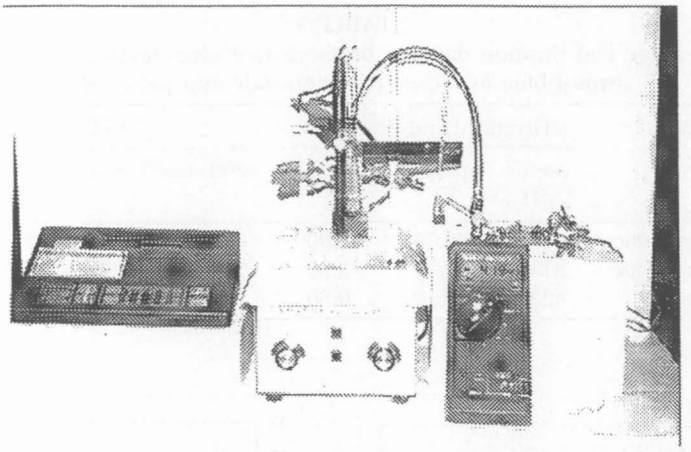


Fig. 7: Experimental set-up for use of portable optical fibre sensor in acid-base titration

For titration between strong acid and weak base, 40 mL of 0.1 M HCl solution was placed in a beaker whereas NaOH 0.1 M solution which was used as a titran was placed in a burette. After adding 5 drops of bromothymol blue in the acid solution, the mixture was stirred by using a magnetic stirrer at a constant speed. The NaOH solution was then added gradually and both readings from the optrode and pH meter were recorded. The same titration process was repeated for other acid-base titrations i.e. titration between strong acid–weak base (0.1 M HCl and 0.1 M NH_4OH) and strong base-weak acid (0.1 M CH_3COOH and 0.1 M NaOH) by using bromophenol blue and thymol blue as an indicator, respectively. The strong acid or strong base was used as a titran in each titration.

RESULTS AND DISCUSSION

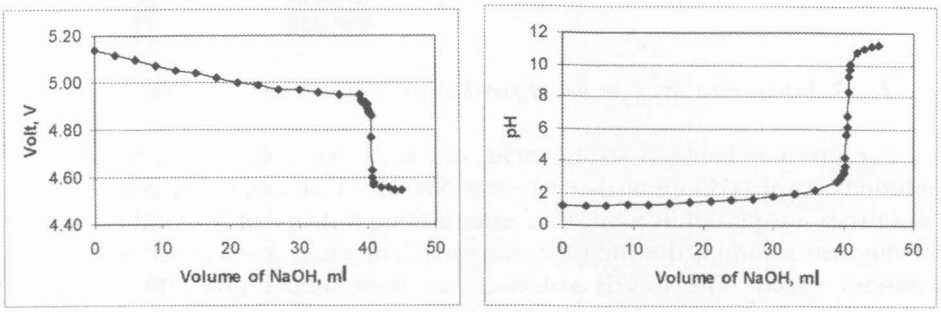
Bromothymol blue, bromophenol blue and thymol blue were chosen in this study because their colour changes (yellow to blue) are suitable for light source used in this study i.e red laser diode. The significant contrast in the colour changes of the indicators used is also important to ensure it could be easily detected by the voltmeter.

The sensor was found to give a rapid response time (in a range of a few seconds) upon changes in the solution pH and this is due to the optical method of measurements with detectors having a sub-microsecond response. Table 1 summarizes the values of pH range as well as the titration end-point for all the indicators used in this study as measured by optrode and pH meters. As shown, the pH range and the titration end-point data obtained from both optrode and pH meters are comparable.

Figs. 8 – 10 show the titration curves for all the acid-base titrations which have been carried out in this study. The voltmeter reading from the optrode was found to change with changes in the solution pH. This change is basically

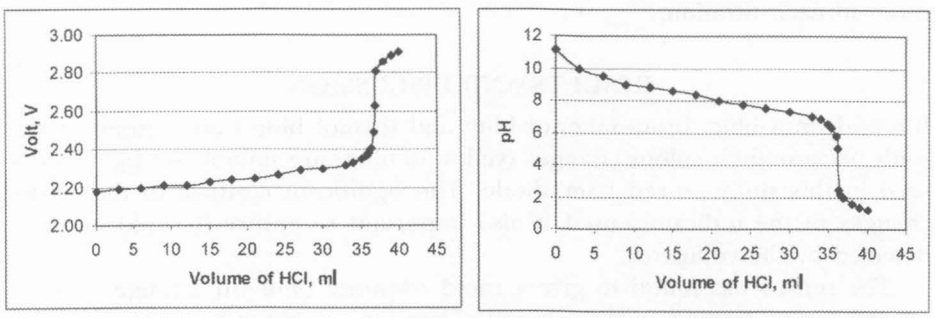
TABLE 1
The pH range and titration data for bromothymol blue, bromophenol blue and thymol blue as measured by optrode and pH meters

pH indicator	Titration End-Point, mL			pH Range		
	meter pH	optrode	different	reference[31]	meter pH	optrode
bromothymol blue	40.70	40.70	0.00	6.0 – 7.6	4.2 – 9.2	4.0 – 8.0
bromophenol blue	37.40	37.70	0.30	2.8 – 5.0	3.0 – 6.2	2.7 – 6.3
thymol blue	42.80	43.10	0.30	7.0 – 9.6	6.8 – 9.4	7.2 – 9.2



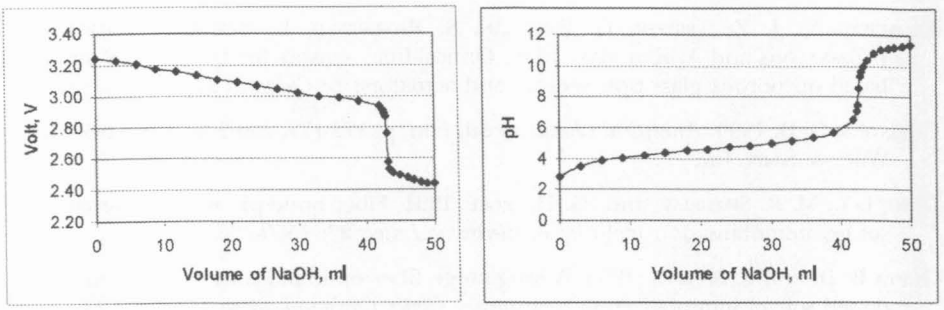
(A) (B)

Fig. 8: Titration curve for titration between 40 mL HCl, 0.1M and NaOH, 0.1M measured by portable optical fibre



(A) (B)

Fig. 9: Titration curve for titration between 40 mL NH_3, 0.1M and HCl, 0.1M measured by portable optical fibre chemical sensor (A) and conventional pH meter(B), when bromophenol blue was used as an indicator



(A) (B)

Fig. 10: Titration curve for titration between 40 mL CH_3COOH, 0.1M and NaOH, 0.1M measured by portable optical fibre chemical sensor (A) and conventional pH meter (B), when tymol blue was used as an indicator

due to the changes in the colour of the solution when the titran was added gradually to the solution. When the end-point of the acid-base titration is reached, the colour change is completed and therefore an abrupt change occurs in the volt reading as shown in *Figs. 8 – 10 (A)*. A similar shape of titration curves was also observed for acid-base titration between HCl and NaOH monitored by optical fibre pH sensor based on reflectance measurement (Moreno *et al.* 1990). These changes correspond to similar changes observed in the pH reading as shown in *Figs. 8 – 10 (B)* when the pH of the solution was monitored by using conventional pH glass electrode.

CONCLUSION

The low-cost portable optical fibre sensor has been successfully developed in this study. The optrode could be used to monitor the progress of liquid acid-base titration between strong acid-strong base, strong acid-weak base and weak acid-strong base. The opto-electronic components used were a laser diode and photodiode detector with no optical filtering elements.

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