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[1] Through convection heat is supplied to the medium and to the supports on which the wire is stretched. In both cases the results depend on temperature differences. In this paper those two will not be studied separately. There is a detailed study of this issue in Mr Cierniak's Ph. D. dissertation [3].

[2] DAS consists of two constant temperature anemometers operating in a differential system [13-14].

FIBER OPTIC pH SENSOR FOR ENVIRONMENTAL APPLICATION

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The paper presents fiber optic pH sensor which is designed to measure pH in the range 4-8 in laboratory as well as environmental conditions. An efficient and simple reagent immobilization procedure is described. The applied procedure combines the ideas of two well-known types of sensing optrode layers: the surface membrane and the bulk one using polymer track membranes (PTM). The microporous polymer foil significantly increases the active surface of the membrane for reagent immobilization and allows to incorporate larger amount of an indicator dye, which enhances performances of the sensor.

1. Introduction

Fiber optic chemical sensors (FOCS) can offer several advantages over traditional sensors. Some of the advantages result from materials used in sensor development *e.g.* dielectricity or possibility of work in network. There are many excellent reviews on FOCS published in recent years [1,2,3]. Although the number of papers on FOCS is increasing, they find limited application. This is sometimes caused by cost of sensor or lack of unified approach to design of the sensor.

There are many types of fiber optic chemical sensors which can measure concentration of neutral or charged species. One of the most important sensors in analytical chemistry is pH sensor. Usually fiber optic pH sensors are based on absorbance or fluorescence indicator. We have used neutral red as the indicator which was immobilized on cellulose acetate membrane. It is assumed that neutral red is immobilized by chemical interaction between the polymer and molecules of the indicator. The colour of neutral red changes from red into yellow in dependence on pH of the solution.

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2. Experimental

2.1 Sensor configuration

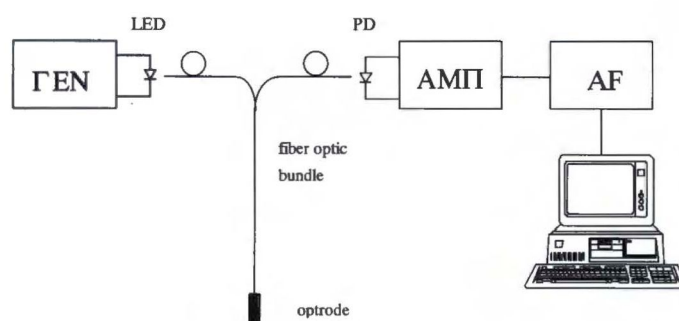The most basic version of the experimental set-up is shown in Fig.1.

Fig. 1. Configuration of fiber optic pH sensors (GEN-square wave generator, LED-light emitting diode, PD-photodiode, AMP-transimpedance amplifier, AF-active filter).

Modulated light from a light emitting diode (LED) is transmitted to the optrode by one arm of the fiber optic bundle. The light matched to the maximum of the molar absorbance of neutral red (560 nm) is reflected in dependence on pH variations and then it is transmitted to a photodiode by the second arm of the bundle. The photodiode is connected with a transimpedance amplifier and active filter. The electrical signal obtained is acquired and processed by a pc-lab card with 12-bit A/D converter. The optrode was built on the common end of the bundle by the use of removable Teflon tube, which holds an optomembrane.

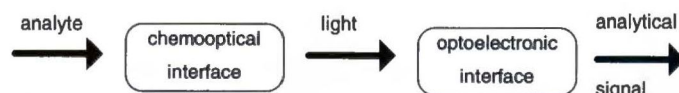Typical conversion process of the signal in the FOCS is presented in Fig.2.

Fig. 2. Conversion of the signal in fiber optic chemical sensor.

Chemical signal caused by the analyte is converted into optical one in chemooptical interface. The chemooptical interface consists of membrane with an appropriate indicator. The indicator changes its optical properties (*e.g.* absorbance, fluorescence) in dependence on analyte. Such an optical signal with information about sample under test is converted into electric signal in an optoelectronic interface. The main part of this interface is the photodetector, such as photodiode or PMT, connected to an electronic circuit. The electric signal is acquired and processed by PC-lab card. Signal is processed according to procedure shown in Fig.3.

The signal from the sensor is acquired by the card, then it is processed according to the calibration procedure and displayed on the monitor. The acquired data can be saved on the disk. In this way a virtual fiber optic pH sensor was built.
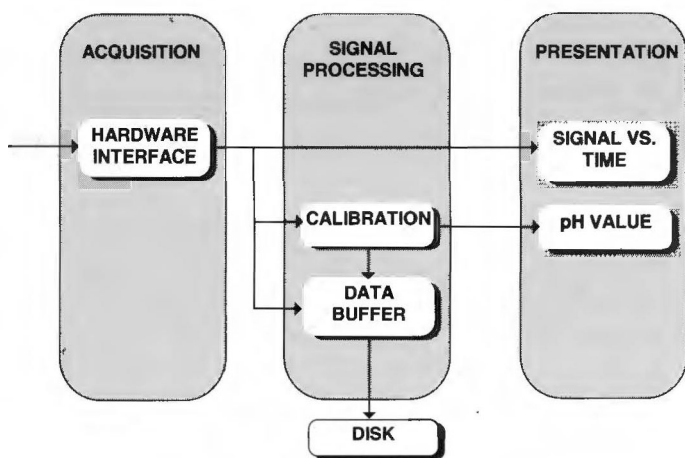
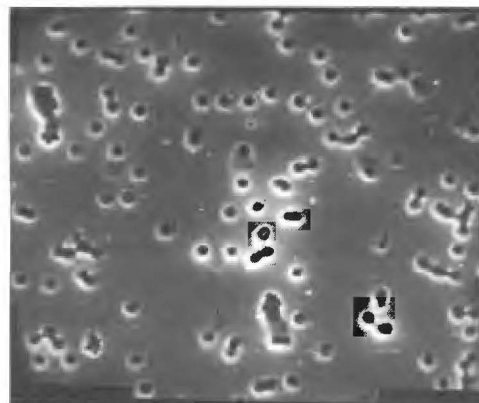Fig. 3. Signal processing in fiber optic pH sensor.

Fig. 4. Photomicrograph of polymer track membrane (PTM) (magnification 6000).

2.2 Immobilization procedure

Development of the immobilization procedure is the basic problem in the design of an optrode. The immobilization procedure should meet several requirements. The reagent used should not be washed out during the measurements. Its optical properties should not be changed and the indicator should still work properly after immobilization. The optomembrane should be compatible with fiber optics and a sample under tests.

Many different types of chemical sensing layers for FOCS have been developed. The techniques lead into two types of the optrode membrane: surface and bulk [4]. The membrane can be prepared as a polymeric foil and then the reagent is immobilized on its surface. It is so-called surface membrane. The second procedure is based on entrapment of reagent molecules in the bulk of the membrane.In such a membrane reversible mass transfer of the analyte from the sample into the bulk occurs. One can expect, that surface membrane should have faster response to an analyte in comparison with the bulk one due to the lack of mass transfer through the membrane layer to the indicator molecules. However, they tend to suffer from a loss of reagent caused by its washing out to the sample under tests.

Our works [5,6] combine two types of membrane preparation using polymer track membranes (PTM). PTM can be made of various kind of polymers: polypropylene, polycarbonate, polyethyleneterephthalate, polyvinylidene fluoride, cellulose esters (nitrate or acetate) etc. The polymer foil is irradiated with high energy ions and tracks after passing ion beams are etched out.Such membranes are commonly used for microfiltration in medicine, biotechnology, electronics. The application of PTM causes the increase of the active surface of the membrane for reagent immobilization and thus increase the amount of incorporated indicator.

Fig. 4. presents photomicrograph of PTM membrane with micropores.

We have used 125 mm thick cellulose acetate membrane (Micro Filtration Systems - Cole Parmer) with porosity of 75% and micropores diameter of 0.8 mm. The cellulose acetate was chosen because of its high water permeability, dye-retaining capability and possibility of the increase of porosity by the hydrolysis of the surface. Due to high porosity PTM has greater surface than a plain membrane (i.e. without pores) [7].

The PTMs were conditioned in the 0.1M NaOH solution over night in order to hydrolyze the foil and enhance its surface porosity. Then, they were immersed into an aqueous-methanolic saturated solution of the neutral red. Afterwards the membranes were removed from the dye bath, cleaned with redistilled water and dried. The obtained membranes were conditioned alternately in the basic and acid solutions, respectively. Then, the procedure of the soaking with reagent was repeated a few times to increase the amount of immobilized reagent. Before the measurements the membranes were kept in the redistilled water at least one day. This method presumes the immobilization of the reagent on the surface of PTM and inside the pores. The applied procedure may be considered as a combination of two different types of sensing optrode layers: the surface and bulk membrane.

3. Results

Designed fiber optic pH sensor was tested during acid-base titrations. The probe was calibrated in typical buffer solutions with pH 4 and 7. We have compared readings of such a virtual fiber optic pH meter with readings obtained from laboratory pH-meter. Comparative results are shown in Fig.5.
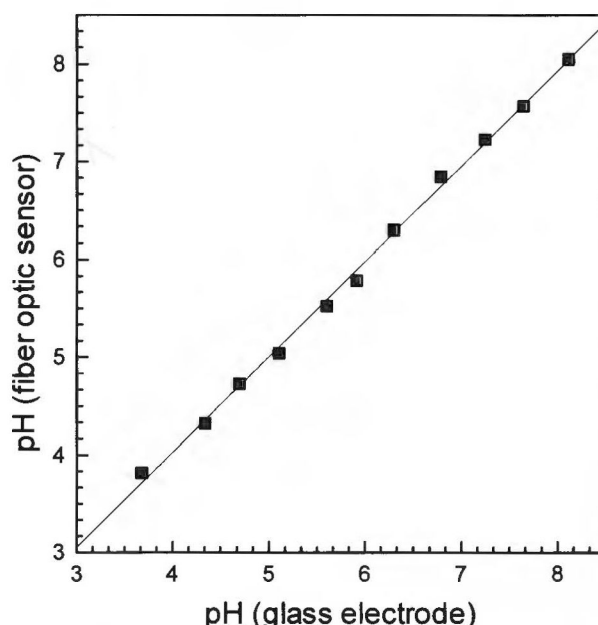

Fig. 5. Comparison of measurements of pH carried out with fiber optic sensor and glass electrode.

Good correlation between this two methods of measurements was observed. The maximum difference in readings was not greater than 0.05 pH. This value can be diminished by increasing the sensitivity of the sensor which can be achieved by use of the membrane with larger amount of the indicator or by increase of the gain of the electronic circuit. The linear range of the sensor based on neutral red was 3.8-8.2 pH. The working range of the indicator was shifted in comparison to its aqueous solution [8] which can be caused by changes of dissociation constant during immobilization procedure. More over, the optrode with neutral red exhibits a wide pH working range especially suitable for environmental monitoring.

The response time of optomembranes was determined by changes of pH from 10 to 2. The obtained results are shown in Fig.6.
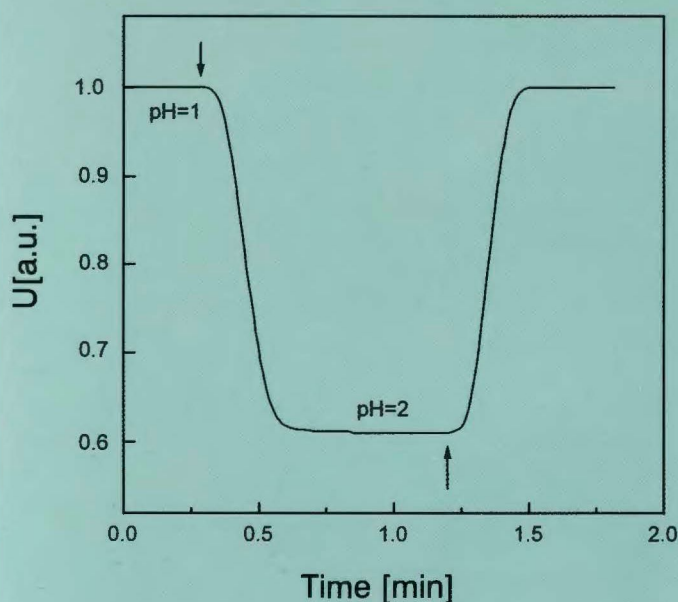

Fig. 6. Dependance of measured signal vs. time during acid-base titrations (arrows mark the addition of appropriate solutions).

The membrane was tested 10 times and reproducible steady state signals were achieved in time less than 30 s. The membrane was kept in distilled water and checked again after 30 days. Comparable results were obtained.

4. Conclusions

Described fiber optic pH sensor can be used in laboratory and environmental measurements. The enhancement of the active surface for reagent immobilization in optomembranes can be achieved using PTM as a matrix. Large amount of the indicator is immobilized due to the combination of two kinds of membranes: bulk and surface. This increases the relative changes of the measured signal. High porosity of PTM leads to the short response time of the optrodes because immobilized molecules of the indicator are easy accessible to the analyte. The applied procedure is quite simple and gives reproducible optomembranes with long-term stability caused by chemical bonding of reagent. Related papers can be found on the internet: http://www.ch.pw.edu.pl/~dybko.

Short biography note

Artur DYBKO obtained a Ph.D. (1996) from the Institute of Electronics Fundamentals of Warsaw University of Technology (WUT); he is a research assistant at the Department of Analytical Chemistry (WUT); he works on fiber optic chemical sensors, optical fibers, laser diodes, optoelectronics.

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