

Optoelectronic system for water quality monitoring

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Abstract. The paper presents a construction of a system for measurements of pH, concentration of calcium ions and concentration of heavy metal ions in water. Three fiber optic sensors in flow configuration were designed and tested. The system is fully automatic and can be used for water quality monitoring.

Key words: fiber optic chemical sensors, automated measuring system, water monitoring.

1. Introduction

Physical and chemical parameters have to be measured in order to assess quality of drinking water [1–6]. The most important parameters can be measured by optical or electrochemical sensors as well. The aim of our work was to design a multiparameter fiber optic measuring system suitable for on-line monitoring of drinking water. Three parameters were chosen: pH, concentration of calcium ions resulting in the hardness of water, and total concentration of heavy metal cations i.e. cadmium, zinc, lead, and mercury.

The aim of this paper is to present recent results on a measuring system for water monitoring.

2. Experimental

2.1. Immobilization of reagents. Immobilization of the reagent is a key issue governing the final properties of the sensor. Various methods of immobilization of a chromoionophore are utilized in optical sensors. The best results are usually obtained if a chemical process is applied. Then the molecules of the chromoionophore are chemically bonded either to the fiber optic or to the polymeric support. Two types of optomembrane can be obtained after reagent immobilization, a so-called surface and bulk [7].

A surface immobilization was applied in this work. An ion exchange resin was chosen as a polymeric support for the chromoionophores. Various types of resins were tested. The best results were obtained for Amberlite resins (XAD4 for pH sensor, IRA 400 for calcium sensor, XAD 4 for heavy metal ions sensor). The procedure of the immobilization started with a solution of an indicator into which polymeric beads were added. Such a mixture was stirred for 30 min and then the solution was decanted. The beads were washed with distilled water until the washings were absolutely free of the indicator. The polymeric beads with the immobilized indicators formed the active phase of the sensors. The beads were placed in a flow cell made of a glass tube, which was then sealed and connected to a pump. The schematic construction of the flow

cell is presented in Fig. 1. Figure 2 presents photographs of flow sensors developed in this work.

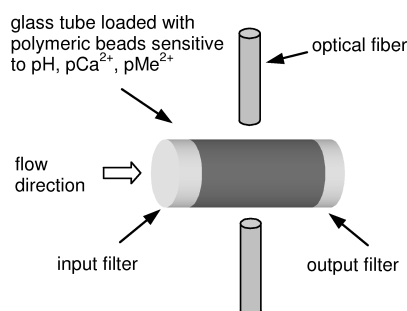


Fig. 1. Schematic construction of a chemical sensor in flow through configuration

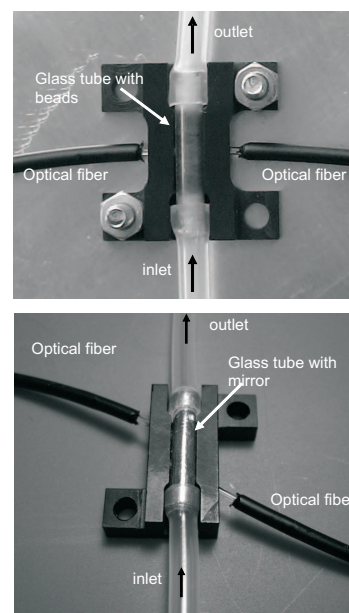


Fig. 2. Optical fiber chemical sensors, a) for pH and calcium ion measurements, b) for heavy metal ion determination

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Having mounted the whole system, the flow cell was washed with water overnight in order to remove this part of the indicator, which was not immobilized. The glass cell was transilluminated by optical fibers mounted in a holder. Three flow through cells were loaded with an appropriate indicator. It was observed that calcium and heavy metal ions sensors generated very low signals, so it was necessary to modify their constructions. It was decided to increase the optical path length of the sensors, which will result in the increase of the sensitivity of the measurements. To achieve this, a glass tube was covered with a very thin layer of silver and protected with a polymeric cover to create a kind of mirror. The optical fibers were placed in some angles in order to increase the optical path within the sensor. Thus the sensitivity of the measurements was increased significantly.

2.2. Measuring set-up. Tests of various chemical sensors require the construction of a system capable of mounting the sensors, which is equipped with appropriate signal conditioning units to fulfil the sensors' specific requirements, allowing data acquisition, visualisation and storage. Moreover, the system should control the work of chemical instruments like a peristaltic pump, a stirrer and so on.

A multi-source unit was constructed with an independent work of three LEDs, which were matched to the analytical wavelengths of the chromoionophores (590 nm or 630 nm for pH sensor – depending on the indicator used, 680 nm for calcium sensor, 510 nm for heavy metal ions sensor). Each of the LEDs was modulated to a square wave, which allows for selective signal detection. The modulation was introduced in such a way that when the LED was switched on, the optical power was maintained constant by the photodiode feedback. The light having interacted with the indicator, possesses information about the concentration of the analyte and then is converted into electrical signal by a photodiode combined with a transimpedance amplifier (OPT 301, Burr-Brown). In the case of the sensor for heavy metal ions it was necessary to design a special lock-in amplifier dedicated to this measurements. The whole measuring system is presented in Fig. 3.

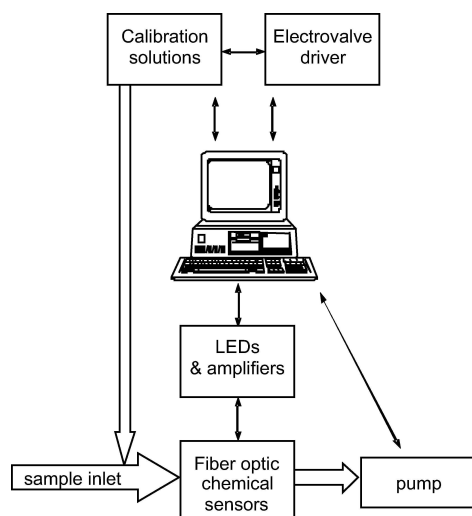


Fig. 3. Measuring set-up

The calibration curve of a sensor is the primary test performed during the measurements. The basic operation required during the measurements is the change of the analyte concentration. This can be done manually by the addition of an appropriate solution but it is time-consuming operation and mistakes by the operator can cause serious errors in the measurements. Thus the calibration procedure was performed automatically. A computer communicates with a set of electrovalves, a combination of which allowed delivering to the sensor the calibration solutions. Having done the calibration, the computer calculates the calibration curve and then a measurement of a real sample is possible.

The data acquisition card (PCI 6025E) with a 12-bit analogue to digital converter was used for the data collection. The card was installed in a personal computer, which work was governed by special application software developed in the LabVIEW environment. The digital outputs of the card were used to control the electrovalves. The pump was connected to the system via an RS 232C interface allowing full control of the instrument.

3. Results

The designed system was tested with solutions prepared in laboratory. All three sensors work independently in a flow condition. The measurement procedure assumes that each sensor is calibrated before the use, and after the calibration procedure the sample is measured. The whole sequence ends with the conditioning solution pumped through the sensor.

3.1. pH sensor. Figure 4 presents calibration curve of the fiber optic pH sensor. This sensor was based on the use of neutral red as an indicator and exhibited the linear range 6.5–7.8. In order to match environmental requirements it was necessary to design the second pH sensor based on bromothymol blue as an indicator (see Fig. 5).

In this case the linear range was equal to 7.7–9.4 pH.

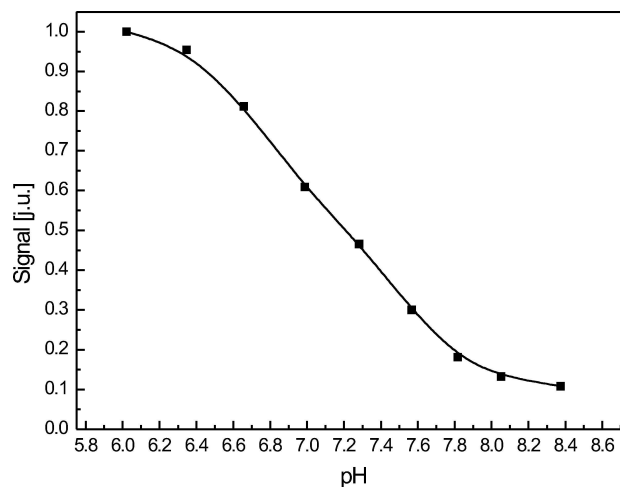


Fig. 4. Calibration curve of pH sensor

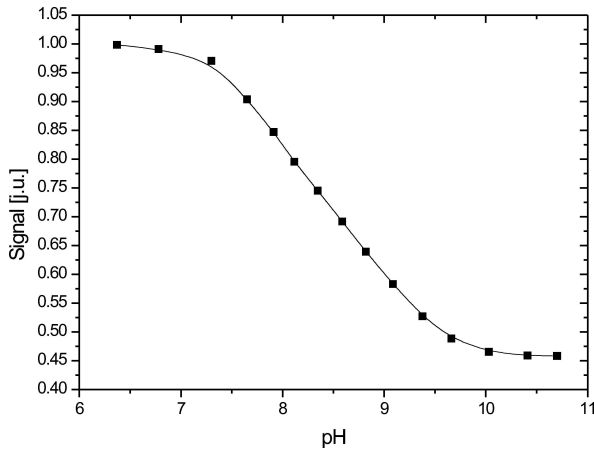


Fig. 5. Calibration curve of an additional pH sensor

3.2. Calcium sensor. Figure 6 shows calibration curve the fiber optic calcium sensor based on Chlorophosphonazo III as an indicator. The sensor can be used in the range of concentrations from 10^{-5} to 10^{-2} M.

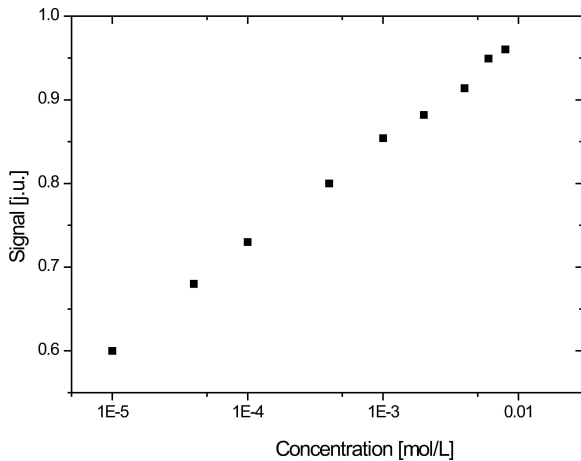


Fig. 6. Calibration curve of calcium sensor

3.3. Heavy metal ion sensor. The indicator used (4-(2-pirydylo) resorcinol) in the fiber optic sensor for heavy metal ions detection was not selective. It was chosen to measure the total concentration of these ions.

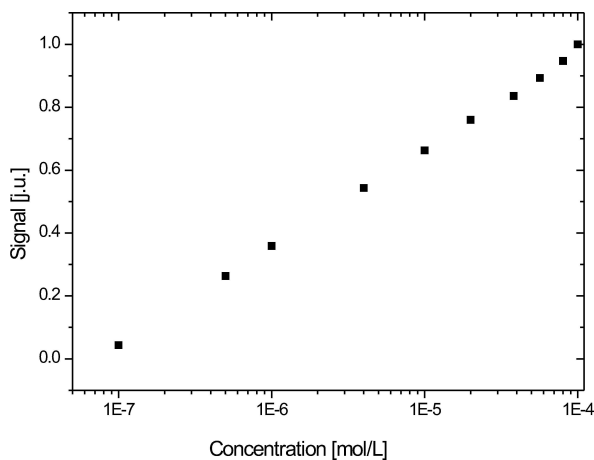


Fig. 7. Calibration curve of heavy metal ions sensor

The calibration curve of the sensor is presented in Fig. 7. The sensor can be used within the range 10^{-7} – 10^{-4} M.

3.4. System performance. The system was tested in a long term monitoring regime. The following accuracy of the measurements were found: pH sensor 0.04, calcium sensor 0.1 pCa, and heavy metal ion sensor 0.1 pMe (where p stands for the power of the appropriate ion concentration). It was also evaluated that system is capable to work without exchange of the sensor for 3 months of continuous monitoring (i.e. 4 measurements per day). After that time the sensors should be regenerated in order to guarantee the above mentioned accuracy.

4. Disussion

A multiparameter measuring system was constructed and tested. The system consists of three fiber optic chemical sensors. The appropriate LEDs were matched to the designed sensors. The sensors were fabricated in a flow through configuration with the use of a polymeric ion exchange resins as a support for the indicator immobilization. The work of the whole system is governed by a computer with software developed in LabVIEW environment. This makes the system capable of on-line monitoring of water quality.

Acknowledgements. The work was financed by a grant of The Ministry of Science and Information Society Technologies No. PBZ-MiN-009/T11/2003.

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