AUTOMATED MEASURING SYSTEM BASED ON OPTICAL SENSORS FOR WATER ANALYSIS

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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.

Keywords: automated system, fiber optic chemical sensors

1. INRODUCTION

Physical and chemical parameters have to measured in order to assess quality of 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 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 principle of the operation of a fiber optic chemical sensor (FOCS) is a chemically sensitive receptor part, which can be called as a chemooptical interface. This interface converts information on the analyte into changes of optical signal. In the case of the designed system, an appropriate reagent exhibiting changes in absorbance is immobilized on a polymeric support in a form of small beads. Such modified polymers are then loaded into a tube in order to construct a flow through sensor.

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

2. EXPERIMENTAL

2.1. Immobilization of the reagents

Immobilization of a reagent is a key issue governing the final properties of an optical 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. Ion exchange resins were chosen as polymeric support for the chromoionophores. Various types of resins were tested. The best results were obtained for Amberlite resins (e.g. IRA 400, IR 45, XAD 1168). 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. A photograph of the flow cell is presented in fig. 1.
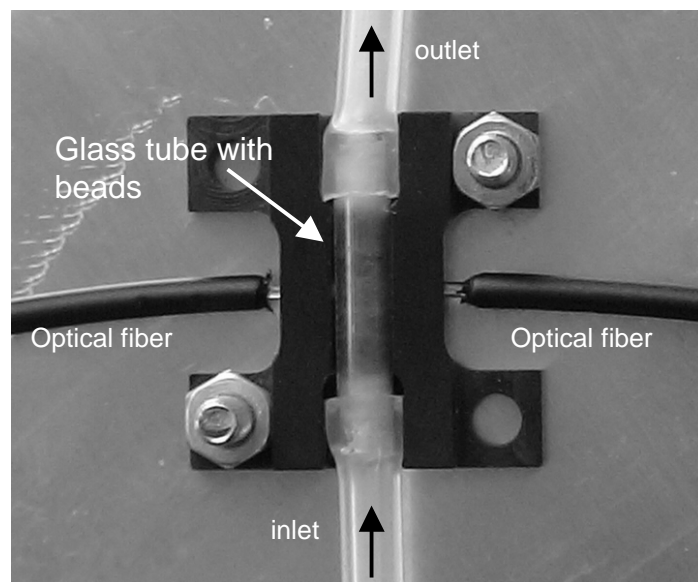

Fig. 1. Fiber optic chemical sensor in flow configuration.

The flow cell was washed with distilled water for 3 hours in order to remove this part of the indicator which was not immobilized on the beads. Also in this way air bubbles were removed from the cell.

2.2. Measuring set-up

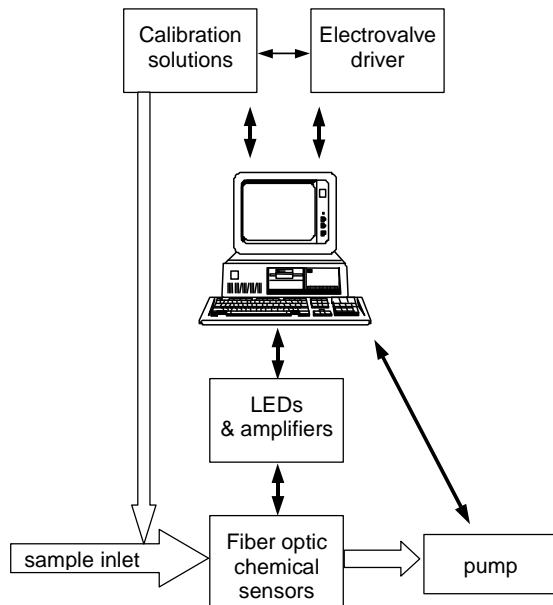A fully automated measuring set-up was designed. The system is schematically presented in fig. 2.

Fig. 2. Measuring set-up.

The system consists of three flow sensors and correlated to them appropriate calibration solutions. The work of the systems is governed by a special software developed in LabVIEW. A multi-light source unit was constructed with an independent work of three LEDs, which were matched to the analytical wavelengths of the indicators used (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).

Each sensor was calibrated before the measurements. This required to pump solutions with various concentration of the analyte. 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 digital outputs of the card were used to control the electrovalves. The peristaltic pump was connected to the system via an RS 232C interface allowing full control of the instrument.

Fig. 3 presents a photo of electrovalves and calibration solutions for one fiber optic sensor.

Fig. 3. Electrovalves and calibration solutions.

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 throught the sensor.

3.1 pH sensor

Fig.4 presents calibration curve of the fiber optic pH sensor.
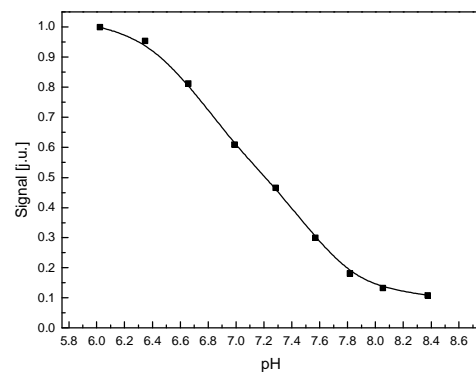

Fig. 4. Calibration curve of pH sensor.

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).
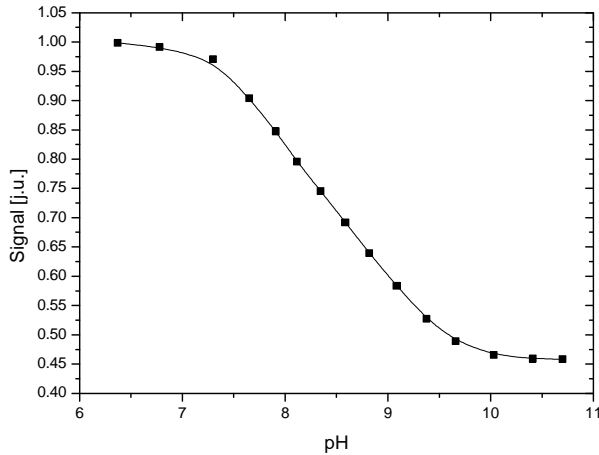

Fig. 5. Calibration curve of pH sensor.

In this case the linear range was equal to 7,7 - 9,4 pH

3.2 Calcium sensor

Fig. 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.
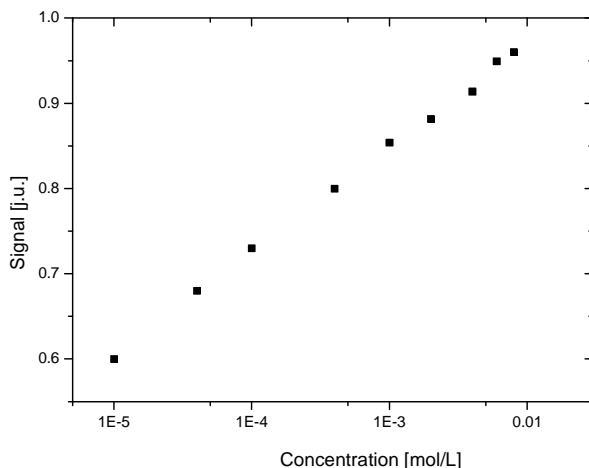

Fig. 6. Calibration curve of calcium sensor.

3.3 Heavy metal ions sensor

The indicator used (4-(2-pirydylazo) 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.

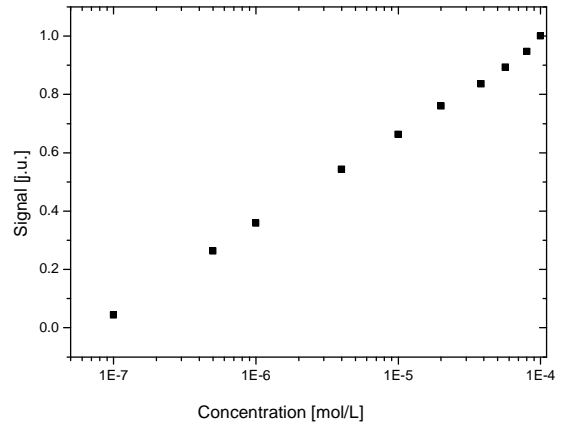The calibration curve of the sensor is presented in fig. 7.

Fig. 7. Calibration curve of heavy metal ion sensor.

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. CONCLUSIONS

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. It is also possible to connect the system to the internet and set up a network of measurement points using LabVIEW tools.

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