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Miniature potentiometric system for determination of H^+ , K^+ , Na^+ , Cl^- , NO_3^- - and Ca^{2+} ions in liquid biological environment

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Abstract. An intelligent potentiometric system for the analysis of liquid biological environments has been developed and researched. The system consists of a set of 6 miniature measuring cells, including polyvinylchloride-membrane electrodes, selective to the presence of H^+ , K^+ , Na^+ , Ca^{2+} , Cl^- , NO_3^- ions in the analyzed solutions, and one central 'reference' cell with a chlorosilver reference electrode. For potentiometric measurements of the voltages of our system, an eight-channel analog-to-digital converter was used, which receives a signal from the down conductor of each of the measuring cells and the central 'reference' cell. This system was tested with aqueous solutions of HCl, KCl, NaCl, $NaNO_3$ and $CaCl_2$ at concentrations from 10^{-1} to 10^{-5} M. This confirmed the usefulness of the developed potentiometric multisensor system for the analysis of the ionic composition of biological environment.

Keywords: potentiometry, potentiometric sensor, ionic composition, miniature system, biological environment, plasticized membranes, multisensor system

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Материалы конференции

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Миниатюрная потенциометрическая система для определения в жидких биологических средах содержания H^+ , K^+ , Na^+ , Cl^- , NO_3^- и Ca^{2+} ионов

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Аннотация. Разработана и исследована интеллектуальная потенциометрическая система анализа жидких биологических сред. Система состоит из набора из 6 миниатюрных измерительных ячеек, включающих мембранные поливинилхлоридные электроды, селективные к присутствию ионов H^+ , K^+ , Na^+ , Ca^{2+} , Cl^- , NO_3^- в анализируемых растворах, и одной центральной «эталонной» ячейки с хлорсеребряным электродом сравнения. Для потенциометрических измерений напряжений нашей

системы использовался восьмиканальный аналого-цифровой преобразователь, на который поступает сигнал с токоотвода каждой из измерительных ячеек и центральной «эталонной» ячейки. Данная система была протестирована с водными растворами HCl, KCl, NaCl, NaNO₃ и CaCl₂ в концентрациях от 10⁻¹ до 10⁻⁵ М. Это подтвердило пригодность разработанной потенциометрической мультисенсорной системы для анализа ионного состава биологической среды.

Ключевые слова: потенциометрия, потенциометрический датчик, ионный состав, миниатюрная система, биологическая среда, пластифицированные мембраны, мультисенсорная система

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Introduction

Ion-selective electrodes are an attractive tool for analyzing the ionic composition of various multicomponent aqueous solutions (which include most biological environment) due to their simplicity of operation, low cost, short analysis time, and the possibility of miniaturizing the sensors and automating the analysis process [1–6].

Ion selective electrodes have been widely used for more than 30 years in a wide range of applications for determining the concentration of certain ions in aqueous solution. The most commonly used ion-selective electrode is the pH electrode [7]. The first pH sensing glass electrode was introduced by Cremer in 1906. Since then wide range of ion-selective electrodes has been developed for the analysis of samples containing many different ions. A chemical sensor is a device which responds to a particular analyte in a selective way through a chemical reaction and can be used for the qualitative and quantitative determination of the analyte [8].

Recently ion-sensors are taking place of various analytical techniques, as they provide a convenient and fast method of electroanalysis. Hence efforts are being made to develop a good sensor for ion sensing which should permit estimation of ion at a very low concentration and have good selectivity and low response time [9]. Advantages of using ion-selective electrodes include their very short measurement time, continuous monitoring ability, measurement of the activity rather than the concentration, and their usefulness in turbid and coloured samples [10, 11].

In this connection, the aim of our work was to develop and test the potentiometric system consisting of a set of 6 miniature measuring cells (MC) including PVC-membrane electrodes selective to the presence of H⁺, K⁺, Na⁺, Ca²⁺, Cl⁻, NO₃⁻ ions (the most common in biological environment) in the analyzed solutions and one central 'reference' cell with chlorosilver reference electrode.

Materials and Methods

Our system was based on the method of direct potentiometry, based on transformation of activity of target ions (H⁺, K⁺, Na⁺, Ca²⁺, Cl⁻ or NO₃⁻, respectively) into electromotive force (EMF), described by the Nernst equation.

Each of the 6 MC included in the developed potentiometric multisensor system and located around the central 'reference' cell (CRC) was a case made on a 3D-printer from PETG filament (see Fig. 1).

This housing was divided inside by a horizontal partition (HP). The lower (next to the HP) section of the case of MC has a volume of 1 ml and three side fittings. One of them (the central one filled with agar-agar with KCl) served as a 'salt bridge' connecting the MC with the CRC. Whereas the other two fittings served to input and output the analyzed solution from the MC and connect the MC to each other.

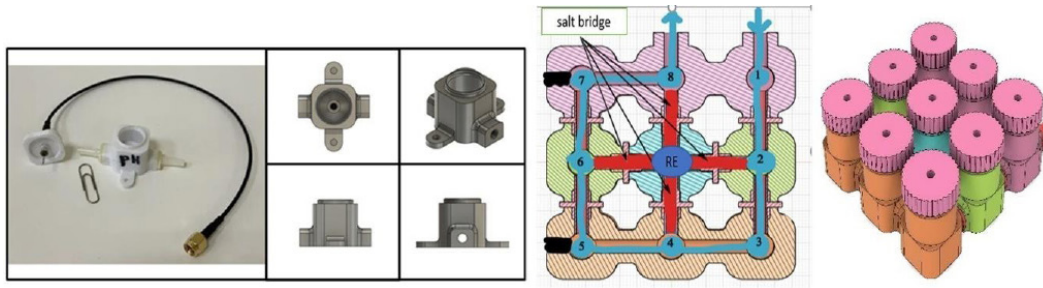


Fig. 1. Scheme of the potentiometric multisensor system developed by us. The device of the measuring cell (MC) is shown on the left; on the right, a diagram of a possible connection of the MC and the central 'reference' cell into a single system (in which two additional MCs are provided for the future expansion of the system with additional sensors)

In the middle of the HP there was a hole, which was sealed with an ion-selective membrane made of polyvinyl chloride plasticized with di-2-ethylhexylsebacinate (DOS), o-nitrophenyloctyl ether (oNPOE), or 2-fluorophenyl-2-nitrophenyl ether (2F2N) with an organic ionophore added during the assembly of the measuring cell.

Then, the upper (with respect to the HP) part of the MC also having a volume of 1 ml was filled with a solution of 2 M KCl - while the lower with respect to the HP part of the MC was filled either with the solution to be analyzed or (between the measurements) with a solution with a given concentration of the ion measured by this MC.

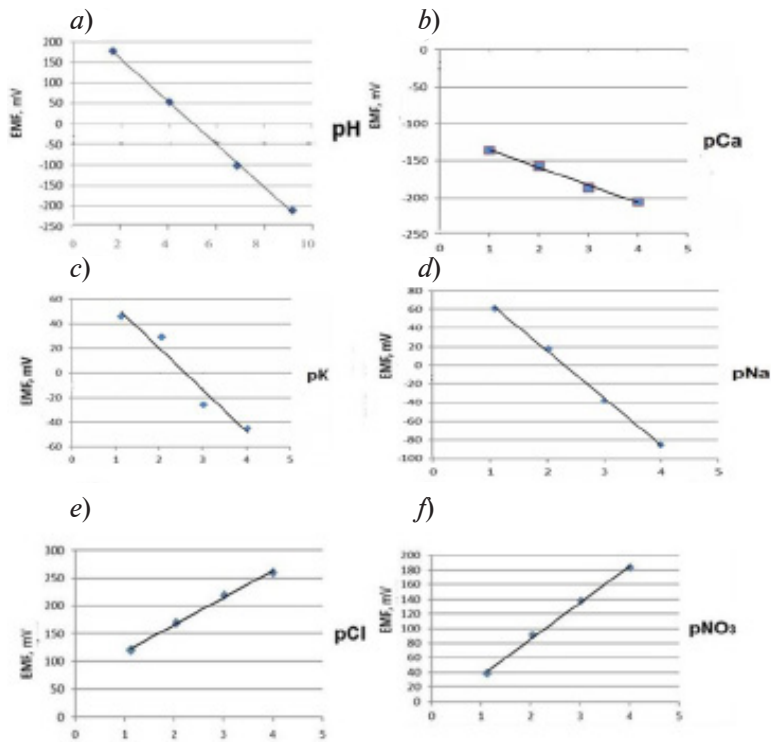


Fig. 2. Graphs obtained during testing of the potentiometric multisensor system developed by us: (a) calibration graph for the pH electrode for buffer solutions with pH 1.65, 4.01, 6.86 and 9.18 (calibration equation: $\text{pH} = 5 - 19 \cdot E_{\text{H}}$); (b) calibration graph for the pCa electrode for aqueous solutions CaCl_2 (calibration equation: $\text{pCa} = -4.64 - 42 \cdot E_{\text{Ca}}$); (c) calibration graph for the pK electrode for aqueous solutions KCl (calibration equation: $\text{pK} = 4.54 - 21 \cdot E_{\text{K}}$); (d) calibration graph for the pNa electrode for aqueous solutions NaCl (calibration equation: $\text{pNa} = 2.3 - 20 \cdot E_{\text{Na}}$); (e) calibration graph for the pCl electrode for aqueous solutions HCl (calibration equation: $\text{pCl} = -1.4 - 20 \cdot E_{\text{Cl}}$); (f) calibration graph for the pNO₃ electrode for aqueous solutions NaNO₃ (calibration equation: $\text{pNO}_3 = -2.86 + 20 \cdot E_{\text{NO}_3}$)

After that, the top of the MC was closed with a cover in which a silver wire, galvanically coated with AgCl and slightly short of the HP, connected to the screened current collector was installed.

The CRC of the developed potentiometric multisensor system had the same case and lid as the MC considered above - only completely filled with 2 M KCl solution, without a HP.

Results and Discussion

At approbation of our developed potentiometric multisensor system, we filled it in turn as the analyzed media with aqueous solutions of HCl, KCl, NaCl, NaNO₃ and CaCl₂ with concentrations 10⁻¹, 10⁻², 10⁻³, 10⁻⁴ and 10⁻⁵ mol/l and also buffer solutions with pH 1.65, 4.01, 6.86 and 9.18. The data obtained in measurements of these solutions confirmed a high sensitivity of the developed MC to the target ions (H⁺, K⁺, Na⁺, Ca²⁺, Cl⁻ or NO₃⁻, respectively) at the absence of such sensitivity to non-target ions, as well as high reproducibility and linearity between values of potential differences between measuring cell and CRC and negative decimal logarithms of molar concentrations of target ions in the whole range of investigated concentrations of these ions from 10⁻⁵ to 10⁻¹ M.

In this case, the resulting calibration equations between the indicated values for the EMF values measured in volts had the form: $\text{pH} = 5 - 19 \cdot E_{\text{H}^+}$, $\text{pK} = 4.54 - 21 \cdot E_{\text{K}^+}$, $\text{pNa} = 2.3 - 20 \cdot E_{\text{Na}^+}$, $\text{pCa} = -4.64 - 42 \cdot E_{\text{Ca}^{2+}}$, $\text{pCl} = -1.4 - 20 \cdot E_{\text{Cl}^-}$ and $\text{pNO}_3 = -2.86 + 20 \cdot E_{\text{NO}_3^-}$, and the original graphs used to calculate the above calibration equations are shown in Fig. 2.

For potentiometric measurements of voltages in our system, an eight-channel analog-to-digital converter (ADC) is used, which receives a signal from the down conductor of each of the measuring cells and the central 'reference' cell. The result of signal processing from the ADC is transferred to a personal computer for further processing.

Conclusion

At approbation of our developed potentiometric multisensor system, having carried out researches of solutions with known concentrations H⁺, K⁺, Na⁺, Ca²⁺, Cl⁻ and NO₃⁻ ions, we have made sure of high enough stability, selectivity and sensitivity of our system in relation to ionic composition of researched solutions. These results confirmed the suitability of our developed potentiometric multisensor system for the analysis of the ionic composition of biological environment.

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