

Application of porous glasses in microfluidic devices

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Nowadays a perspective appears of applying porous glasses in microanalytical devices. The opportunity of application of porous glasses as optical sensors has been shown in the present paper. Preliminary results of studying the electroosmotic flows through porous glasses are discussed.

Keywords: porous glasses, diffusion reflection spectroscopy, microfluidic, electrokinetic, electroosmosis.

1. Introduction

One of modern directions of analytical instrument-making development is the creation of devices based on a microchip platform [1–5]. Such devices are called μ -TAS – micro total analysis systems or laboratories on a chip (Lab-on-a-Chip). The advantages of these systems as compared to conventional analytical devices include: limitedly small volume of samples being analysed and reagents being used, possibility of control and automation of all analysis stages, compactness, low power consumption, *etc.* [6]. The main element of such systems is the analytical microchip. At least two types of microchips based on the use of micro- and nano-technologies are known: matrix (hybridised) [7] and microfluid (nanofluid) chips [8, 9]. Matrix chips are based on the use of local immobilization of selectively sensitive substances (receptors) on a small area of inert substrate, which allows to perform a qualitative express analysis. In microfluidic chips (MFC), functional elements and devices are disposed on a small area, *i.e.*, mixers, heating chambers, filters, reaction chambers, separating devices, fraction collection chambers, sensors, pumps, *etc.* Such chips allow one to perform actions with microquantities of the sample, namely: injections, sample dosing, mixing with reagents, specific reactions, separation of the obtained product into components, detection and registration of components. MFC can be used not only as devices for complex substance analysis in real time but also as devices for synthesis of new compounds.

Porous structures, in particular porous glasses (PGs), can be referred to prospective functional elements for MFC [10–12]. Due to their unique physical and chemical characteristics, PGs are successfully used in conventional analytical devices, such as filters, columns, reactors, *etc.* and as electroosmotic pumps [13]. Modern technologies allow one to create PGs with through nano-sized pores (from 2 nm to 500 nm) with known structural and chemical characteristics [14]. Excellent optical properties of PGs allow using high-sensitive detection methods at registration of sample components in PG. This report contains preliminary research results for PGs manufactured from DV-1Sh glass as functional structures for MFC.

2. Experimental studies

Samples of DV-1Sh two-phase glass, MIP (according to electronic microscopy data, the average pore radius $r_{\text{ave}} = 5.5$ nm, porosity $W = 24\text{--}26\%$) and MAP ($r_{\text{ave}} = 44\text{--}54$ nm, $W = 40\text{--}43\%$) porous glasses with the thickness of 0.5 mm were obtained from it have been investigated.

Diffused reflection spectres of glasses have been measured on the Hitachi U-3410 spectrophotometer (Japan). The measurements were carried out at the scan rate of 120 nm/min and spectral slot width of 2 nm. The measurements of glass reflection indicatrices were conducted on an experimental installation with the AOS-1 acousto-optical spectrometer (wavelength 632.8 nm).

Electrokinetic studies were performed on the MFC simulator. In doing so, a precision programmable voltage source PUIN-MFAS (IAI RAS, Russia) was used.

2.1. Optical measurements – PG reflectivity

The results of measurements of diffused reflection spectres for DV-1Sh two-phase glass, porous glasses (MIP, MAP) and PG with rhodamine B molecules being embedded into them have been used at calculation of Gurevich–Kubelka–Munk (GKM) functions [15] and are given in Fig. 1. It follows from the relations obtained that the initial DV-1Sh glass has a smaller light scattering than PG in the whole spectral range of measurements, and a minimum of the GKM function for it is observed in the interval of 360–370 nm. In PG, the light scattering significantly prevails over absorption. A minimum of the GKM function falls in the range of 520–540 nm for PG MIP and in the interval of 580–600 nm for PG MAP. We have to note that in the range from 300 nm to 550 nm, MIP glass has larger light scattering than MAP. In doing so, a local maximum of the GKM function has been revealed for MIP in the region of 380–390 nm. The embedding of rhodamine B molecules into PG leads to a transformation of the GKM function; for example, for MIP glass, an expressive local peak appears with the maximum at 555 nm (rhodamine B absorption wavelength), and for a MAP sample, a variation of spectral dependence in the rhodamine absorption area takes place. So, using diffuse reflection spectroscopy, one can perform registration of molecules with a typical absorption band in PG.

When optical methods are used for detecting an informative signal in microfluid systems, the selection of aperture and light flux registration angle is important. PGs have a high light scattering, and when they are used in MFC glass, the surface treatment has to fulfil special requirements. It leads to the situation when the presence of diffuse and mirror components of reflection takes place during the light flux reflection, which should be taken into account in selecting a registration scheme. Therefore, measurements of the reflection indicatrix for glasses have been conducted at light incidence angles $\alpha = 0^\circ$ and $\alpha = 30^\circ$. Figure 2 shows the results for the angle $\alpha = 0^\circ$. As a consequence, the reflection indicatrices differ from lambertian ones, have the mirror component and the reflection indicatrix for DV-1Sh glass has a rather complicated shape.

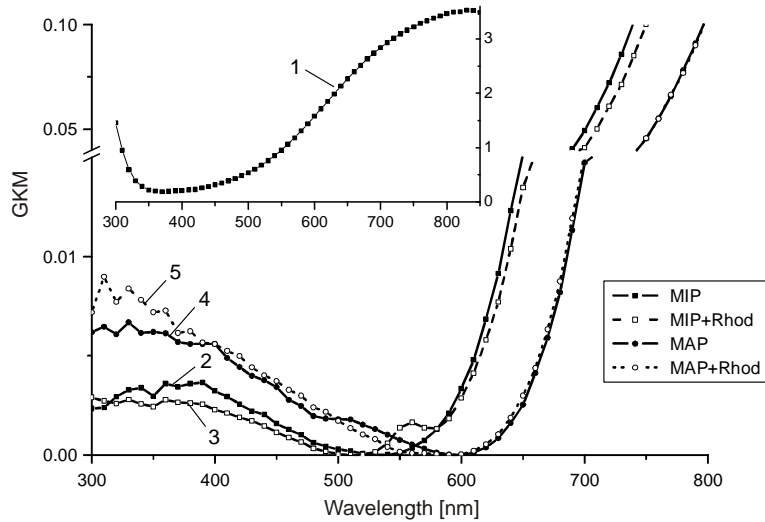


Fig. 1. The function of Gurevich–Kubelka–Munk for two-phase glass DV-1Sh (1), PG MIP (2) and MAP (4) and for PG with adsorbed molecules of rhodamine B (MIP – 3, MAP – 5).

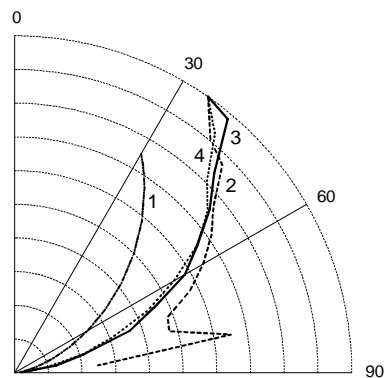


Fig. 2. Indicatrixes of reflectance for DV-1Sh and PG MIP and MAP (wavelength 632.8 nm). 1 – lambert indicatrix; 2, 3, 4 – indicatrixes for DV-1Sh, MIP and MAP $\alpha = 0^\circ$.

2.2. Electrokinetic measurements

The objective of this series of experiments was to evaluate the electroosmotic flow (EOF) arising in the pore space of glasses under the effect of electrical field. The electroosmotic flow is caused by the appearance of a double electrical layer at the liquid-solid interface when an electrical field is applied. In case of contact with an electrolyte solution, negative charges are generated on the glass surface due to dissociation of silanol groups. The mobile diffused layer with an excess of cations is retained by electrical interaction forces but the attraction forces decrease when the distance from the interface grows, thermal motion prevails and the concentration of cations in the diffused layer tends to the total concentration in the electrolyte volume. Under the action of electrical field, the diffused layer with an increased cation concentration moves towards the cathode entraining the remaining fluid mass in the pore (due to molecular adhesion and internal resistance), which forms the electroosmotic flow. EOF is present in all electrokinetic methods as one that can never manage to fully exclude the appearance of surface charges. EOF control allows to achieve accurate and reproducible analytical results in using PGs in MFC.

Electrokinetic measurements were conducted on an MFC simulator (Fig. 3). The construction consisted of two polymer plates, each with a through channel and a reservoir (3, 5) for fluid. Platinum electrodes (2) were placed in the channel. PG (4) was fixed between the plates, at the area of channel combination. The channel and reservoirs were filled with a 0.01 M borate buffer pH 9.2. Before installing into the construction, PG was impregnated with the buffer solution. Then the voltage (10 V) was applied on the electrodes. In doing so, the current passing through the channel and through the PG was registered.

Initially, the channel and reservoirs were filled with a buffer with the same concentration. It was supposed that the main process determining the fluid flow in the channel would be electro osmosis and the current value would be constant. As a result of experiment, a monotonously decreasing kinetic dependence was obtained for the current value and a considerable mass transfer was observed, due to which

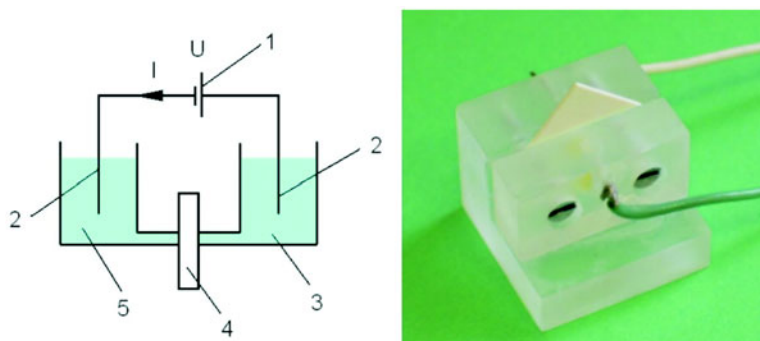


Fig. 3. The MFC simulator. 1 – the source of voltage, 2 – electrodes, 3 – reservoir for buffer with concentration C_1 , 4 – PG, 5 – reservoir for buffer with concentration C_2 .

a pressure was generated creating the counter-flow. In order to eliminate this effect on the measurement results, the normalisation of the data obtained in respect of the initial measurements was performed with the same buffer concentration. With the insertion into the anode reservoir the buffer with a higher concentration than in the channel and in the cathode reservoir, a diffused flow appeared, which is caused by the concentration difference, and with the application of voltage on the electrodes – the electroosmotic flow was additionally generated. The direction of these flows coincided, which caused a fast fluid mass transfer into the cathode reservoir. In the case of anode space filling with a buffer solution with a lower concentration than in the channel, the diffused component impeded the electroosmotic flow. The measurement results are given in Fig. 4. With the general similarity of mass transfer processes, a faster kinetics caused by a larger pore size was observed in MAP glass. EOF mobility for the borate

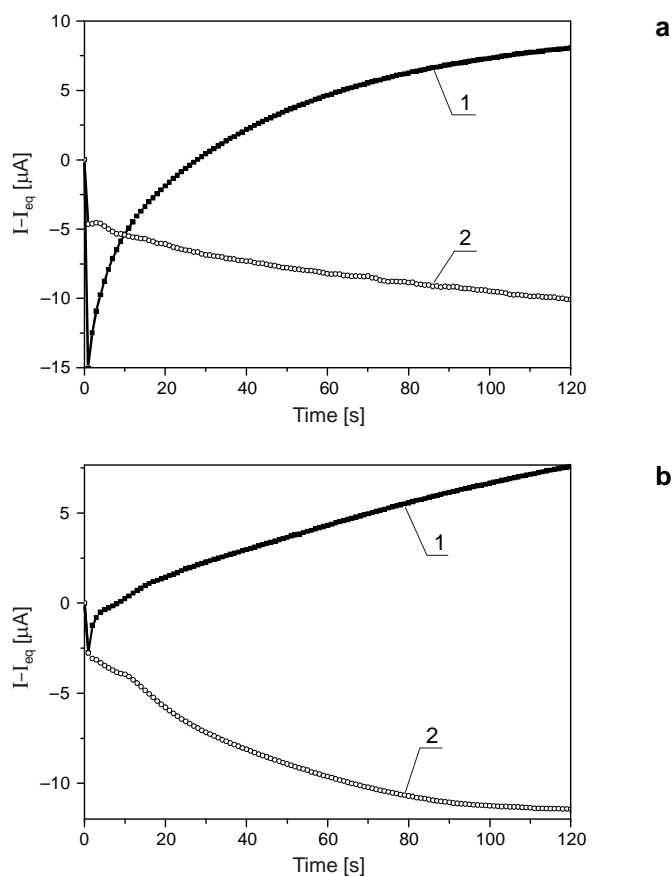


Fig. 4. The kinetic dependences of current $I - I_{eq}$ in PG MIP (a) and MAP (b) at concentration of the buffer in anode area, PG and cathode area: C , $C/4$ and $C/4$ (curve 1), $C/4$, C and C (curve 2) – a; $C/2$, $C/4$ and $C/4$ (curve 1), $C/4$, $C/2$ and $C/2$ accordingly (curve 2) – b. I_{eq} – current strength through the cell with a buffer solution of equal concentrations: $C/4$ (curve 1) and C (curve 2) – a, $C/4$ (curve 1) and $C/2$ (curve 2) – b.

buffer pH 9.18 in pores of PG MAP is equal to $\mu_{PG} = 1.50 \pm 0.15 \text{ cm}^2/(\text{Vs})$ ($n = 10$, n – the number of experiments from which the estimation was obtained).

For PG MAP, the measurements of the current with the introduction of a borate buffer solution containing a rhodamine B dye into the anode area were conducted. According to the authors [16–18], rhodamine molecules used in the buffer are not charged; therefore, they should not exert any essential influence upon the current variation.

However, the results evidence that the addition of rhodamine has led to an increase in the current value at the initial section (12 c). rhodamine molecules were fixed well in glass pores, so that one could not manage to wash them out from there, either by a hydraulic flow or by an electrokinetic flow. This effect allows to use PG with the indicator complexes embedded into the pores or adsorbed labelled structures (for example, antigens or antibodies) as sensor elements with stable characteristics, which can be integrated into the microfluidic chip channel.

As a result of adding the rhodamine B into the solution, the EOF mobility in the PG MAP pores grows ($\mu_{PG + rhod} = 2.90 \pm 0.05 \text{ cm}^2/(\text{Vs})$, $n = 4$).

Electrokinetic processes in PG also lead to heating of the fluid passing through the pores. The evaluations obtained according to approximate formulae at the voltage of 10 V on electrodes give the heating value $\sim 1 \text{ }^\circ\text{C}/\text{min}$. This value is sufficient for variation of the parameters of flow passing through the pores.

3. Discussion

The most essential functional elements of microfluidic devices (where it is possible to use porous structures) are the systems for generation of controllable microflows, separation of the sample into components, detection of the analytes, preliminary sample preparation (for example, filters). The use of PG as filtration elements is probably not justified. But PG can be successfully used as electroosmotic pumps, devices for micro-electro-chromatographic separation of the sample into components and as sensor devices. An evident advantage of PG in these cases is a possibility of forming porous structures with specialized physical, chemical and structural characteristics as well as giving PG the required geometrical shape for embedding it into MFC.

The MAP glasses, which have a greater porosity and pore sizes and enable us to produce controllable flows with comparatively low voltage, can be the most suitable for solving the majority of analytical problems as an electroosmotic pump. MIP glass can be used for taking an analyte sample from the flow. However one should bear in mind that small pore sizes with MIP can lead to their fast *clogging*. In addition, the homogeneity of the liquid medium being used is also important, because for the multicomponent composition different components move in the pores with different velocities. So charged particles in the solution have electrophoretic

phenomena and produce the flow potential in the direction of movement through the pores. Therefore, the most expedient use of electroosmotic pump is generation of buffer flows for further analyte and reagent transportation.

As a sensor element with embedded indicator complexes, both MIP glass and MAP glass can be used identically. Indicatrixes of reflection for these glasses are similar. Apparently, the major design consideration will be a possibility of introducing the indicator complex being selected into the porous space, preserving its properties and assuring analyte access to the complex being introduced.

4. Conclusions

Diffuse reflection spectra for MIP and MAP porous glasses as well as rhodamine B adsorbed in PG matrixes allow us to make a conclusion about adaptability of optical detecting of the molecules with a typical absorption band.

The measurement of the indicatrix of light reflection from the PG surfaces allows us to select the most suitable geometry for the optical registration system.

The obtained electrokinetic dependences have shown that faster processes occur in MAP, apparently, due to the larger pore sizes. The introduction of rhodamine B molecules in the matrix changes the electrokinetic properties.

The rhodamine B complex adsorbed in the PG matrix is stable and is not washed out, which allows one to use PGs as sensitive elements.

Thus PGs can successfully be used as electroosmotic pumps, devices for micro-electro-chromatographic separation of the sample into components and as well as the sensor devices for MFC.

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