Study of the separation processes of gases in the microchannel based on the stochastic simulation

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Abstract. One of the main problems in the development of microfluidic gas chromatography columns is the complexity of the preliminary modelling of the microfluidic systems, namely, the complex modelling of physicochemical processes on the inner surface of the microchannel walls and the simulation of carrier gas movement. The purpose of this work is to develop an integrated computer model for the separation of sample gas components in a gas chromatographic column that takes into account the effect of the carrier gas on the gas-sample particles and adsorption processes in the surface layer. The proposed model is based on stochastic method. The simulation results can be used to improve the development of microfluidic gas chromatography columns and other devices in which the separation of gas mixtures occurs.

1. Introduction
Modern microfluidic devices are widely used in analytical chemistry for dosing, transportation, separation of the widest range of substances. Over the past ten years in high-performance gas chromatography, dosing devices [1-5] and separation columns [6-8], based on microfluidic systems and allowing to work in nano-litre eluent flow ranges are widely used. A microfluidic device operating as a separation column is a microchannel implemented on the surface of a glass or silicon wafer inside which the sample gas propagates under the influence of the carrier gas. The separation of the sample gas components occurs due to their different interaction with the sprayed on the inner surfaces microchannel walls sorbent. Analysis of the operation of such devices for the study of the chemical composition of the gas shows that the use of microfluidic technologies makes it possible to create portable analytical instruments whose sensitivity reaches 0.5 ppbv and the time of one analysis cycle is reduced to 0.2 min [9]. However, the development and manufacture of microfluidic devices are associated with a number of technical and methodological problems that are not completely solved yet. At present, polymer technology and technology based on splicing of structured silicon and glass plates are most widely used for the manufacture of microfluidic devices. However, the first method cannot be applied when using high temperatures or corrosive media at the manufacturing stage, and the cost of the second is relatively high due to the use of expensive equipment in its implementation.
The main methodological problem in the design and manufacture of microfluidic devices is the difficulty of modelling the physicochemical processes occurring inside the channel and in the surface layer near its inner walls. This problem is due to the following main factors:

- the presence of heterogeneity and irregularity of the flow at the bend of the channel;
- the influence of the microroughness of the inner surface of the channel on the behaviour of the sample gas particles and the complexity of modelling this effect;
- the complexity of the mathematical description of adsorption processes in the surface layer of a microchannel;
- the characteristic size of the channel is of the order of tens micrometres, therefore, it cannot be guided only by a macro approach while modelling of the processes occurring during the flow of sample gas inside the channel, especially near the surface layer.

Creating an integrated computer model would solve the problem of optimizing the design of the microfluidic device and the optimal choice of the analysis mode even before the design and technological work. Thus, the purpose of this work is to develop an integrated computer model for the separation of sample gas components in a gas chromatographic column based on a microfluidic device that takes into account the effect of the carrier gas on the sample gas particles and adsorption processes in the surface layer. To achieve this purpose, the following tasks were set:

- to develop a method for modelling of the separation of sample gas components, taking into account the movement of sample gas particles under the influence of the carrier gas velocity field and the movement of sample gas particles in the near-surface layer of the channel, taking into account adsorption processes;
- to develop a computer model based on the proposed methodology;
- to conduct a series of numerical experiments on the separation of the components of the sample gas, confirming the efficiency of the developed model.

In this work, the Navier-Stokes equations are used to calculate the carrier gas velocity field. The description of the particle behaviour in the near-surface layer is based on the stochastic approach, while the set of distributions of random values determining the behaviour of the sample gas particles is calculated preliminarily using the molecular dynamics method.

2. Development of methodology for modelling separation processes

2.1 Main features of gas chromatography

The field of analytical chromatography is limited to the use of physicochemical processes for the separation of mixtures of substances that occur in heterophase systems [10]. In gas chromatography, a carrier gas is used as the mobile phase, and the stationary is a solid sorbent or liquid deposited on the inner surface of the chromatographic column. Depending on the used type of stationary phase, gas chromatography is divided into gas adsorption and gas-liquid chromatography. In the first case, the stationary phase is a solid carrier (silica gel, coal, aluminium oxide), in the second, a liquid deposited on the surface of an inert carrier. This paper deals with gas adsorption chromatography, where the test substance has a gaseous aggregative state. In the considered systems, the following processes occur:

1. adsorption - the phenomenon of concentration of a substance at the interface,
2. desorption is a reverse adsorption phenomenon,
3. absorption - the phenomenon of the predominant distribution of a substance in the volume of one of the contacting phases,
4. diffusion - the phenomenon of penetration of particles of one substance into another at their contact,
5. self-diffusion - a special case of diffusion, in which the own particles of a substance diffuse.

The method of gas chromatography has a number of characteristics features:

- the process of free sorption is used, when the nature and density of the carrier gas has practically no effect on the retention of the substance, in other words, the chemical interaction of the carrier gas with the stationary phase (sorbent) and sample components are excluded;
- the interaction of the sample gas with the stationary phase has an adsorption character due to intermolecular interactions;
- separation of the mixture occurs due to the different ability of its components to interact with the stationary phase;
- the probability of interaction between the sample gas particles is extremely small due to their low concentration.

The above conditions were used in the development of the methodology for simulating the separation of a gas mixture inside a microfluidic gas chromatographic column.

2.2. The main provisions of the developed model
To develop a model for the separation of sample gas components, the following preliminary calculations must be made:

1. the calculation of the stationary solution of the velocity field of the carrier gas using one of the application programs, for example, ANSYS or Comsol Multiphysics, while the calculation is carried out on the basis of the Navier-Stokes macroscopic equations that treat the gas as a continuous medium;

2. calculation of the set of distributions of random values $P_{\vec{v}_{out}}(A_i)$, describing parameters of desorbed particle for each component of the sample gas $A_i$, such as a vector of the return velocity $\vec{v}_{out}$ and the time spent near the wall (retention time) $\tau$, on the basis of molecular dynamics method.

To calculate flow parameters in simple channels, the Navier-Stokes differential equations system is used, which does not take into account the molecular nature of gases and liquids and treats them as a continuous medium, described from the point of view of spatial and temporal changes in density, velocity, pressure, temperature and other macroscopic parameters. The flow continuity model is easier processed mathematically than alternative molecular models, allowing the use of differential calculus. The Navier-Stokes equation for this case is given below:

$$\rho(\vec{\nabla} \cdot \vec{v}) = \nabla \cdot \left[-pI + \mu(\nabla \vec{v} + (\nabla \vec{v})^T)\right] + F,$$  \hspace{1cm} (1)

where $\rho$ is the flow density [kg/m$^3$], $p$ is the pressure inside the channel [Pa], $\vec{v}$ is the velocity field [m/s], $\nabla$ is the operator nabla, $F$ is the external specific force [N/m$^3$], $\mu$ is the dynamic viscosity coefficient [Pa·s], $I$ is the identity tensor, $T$ is the absolute temperature [K].

To calculate the set of distributions of random values $P_{\vec{v}_{out}}(A_i)$, a software complex based on the molecular dynamics method was used. The physical interpretation of the model is shown in Figure 1.

![Figure 1](image-url)  
**Figure 1.** The Physical interpretation of the model of the behaviour of particles in the surface layer: PBC – periodical boundary conditions.

Model parameters:
- interaction according to potential of Lennard-John 6-12:

$$U = 4\varepsilon \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6,$$  \hspace{1cm} (2)

where $\varepsilon$ is the equipotential well depth [J], $\sigma$ is the characteristic van der Waals molecule diameter [m], $r$ is the the distance between particle centers [m];
- periodic boundary conditions along the X and Y axes (parallel to the surface), elastically reflecting boundary along the Z axis;
- the surface is presented in the form of fixed overlapping spheres.

Setting up the experiment:
1. in the zone of generation of test particles, a particle is initiated with a given energy parameter and approach angle to the simulation cell (relative to the normal to the surface);
2. the trajectories of motion of all particles of the system are calculated;
3. when the particle reaches the adsorbed state, the retention time begins (if the particle enters this area several times, the times are summed);
4. the simulation ends when the test particle reaches the upper boundary of the simulation cell.

The output data of the experiment are: the retention time (being in the adsorbed state); particle return time; angle of return (relative to the normal to the surface); total energy.

Processing Results:
1. the experiment is carried out from $10^2$ to $10^5$ times;
2. build the distribution of the output data depending on the angle of approach and the initial energy of the particle.

Further, the output data values are assigned a probabilistic character, normal distributions are constructed with the mathematical expectation and variance obtained from previous calculations based on the molecular dynamics method. The probabilities of adsorption $P_{ad}$ and desorption $P_{des}$ are calculated on the basis of the output of the experiment.

The results of the above calculations – the velocity field of the carrier gas $\mathbf{U}$ and the set of distributions of random values $P_{\mathbf{v}_{\text{out}}}(A_i)$, are the initial data for building a complex model that describes the behaviour of the sample gas in the microchannel microfluidic gas chromatography column. The structural diagram of the developed model is presented in Figure 2.

**Figure 2.** Block diagram of the model being developed: $\mathbf{U}$ – field-velocities of the carrier gas, $P$ – set of distributions of random values $P_{\mathbf{v}_{\text{out}}}(A_i)$ that determine the behaviour of sample gas particles in the near-surface layer.

As mentioned earlier, a microfluidic device operating as a separation column is a microchannel implemented on the surface of a glass or silicon wafer inside which the sample gas propagates under the influence of the carrier gas. The separation of the sample gas components occurs due to their different interaction with a sorbent sprayed onto the inner surfaces of the microchannel walls. The geometrical representation of the developed model is presented in Figure 3.
According to the geometrical representation of the developed model, sample gas particles (yellow) with a diameter d of the order of angstrom are located in a microchannel filled with a carrier gas (green) with a certain velocity field. The diameter of the microchannel D is tens of micrometres. A sorbent is applied on the inner walls of the channel, which forms the border area (pink). The border area is conventionally divided into elementary cells. When particles of a sample gas get into them, the calculation of the parameters determining the further behaviour of the sample gas particles is started, based on the previously obtained set of distributions of random values $P_{v_{out}}(A_i)$, of the parameters, individual for each type of particle. In this case, for a particle there are three variants of the behaviour when a surface layer enters the cell: 1) a particle is reflected from a wall with the velocity vector $v_{out}$, determined by the set of distributions of random values; 2) the particle is adsorbed and is in the cell until the end of the simulation cycle; 3) after adsorption through the residence time near- the wall $\tau$ and after passing the distance l along the channel wall, the particle is desorbed with the velocity vector $\vec{v}_{out}$, while all of these quantities are determined by the set of distributions of random values.

In this paper, the stochastic approach is used to describe the behaviour of sample gas particles inside a microchannel due to the minimal complexity of computer calculations and the satisfactory accuracy of the results obtained.

The essence of the stochastic approach to modelling of gas-dynamic systems is that the influence of the microchannel structure and the carrier gas on the sample gas is assigned a probabilistic character. In the case of the description of the influence of the carrier gas flow on the movement of the sample gas particles, it looks as follows: the carrier gas flow profile sets the preferred direction of the sample gas flow, while the velocity of each sample gas particle is random in the stationary case (along the Y and Z axes) corresponding to the Maxwell distribution:

$$\frac{\Delta n}{n \Delta v} = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}},$$

with the most probable speed:

$$v_p = \sqrt[3]{\frac{2k_B T}{m}},$$

where $\frac{\Delta n}{n \Delta v}$ is the the proportion of molecules with speeds in the diapason $\Delta v$ [m/s$^2$], $m$ is the molecular mass [kg], $k_B$ is the Boltzmann constant [J/K], $T$ is the absolute temperature [K].

The directional movement of the sample gas particles along the X-axis along the cylinder axis is due to the pulsed interaction with the carrier gas particles:
\[ m_{pk} v_{pk,i} = m_{pk} v_{pk,i-1} + m_g v_{g,i-1}, \]  

where \( m_{pk} \) is the k-type particle mass of sample gas [kg], \( v_{pk,i} \) is the k-type particle velocity of sample gas at the i-th moment of time [m/s], \( m_g \) is the particle mass of carrier gas [kg], \( v_{g,i} \) is the particle velocity of carrier gas at the i-th moment of time [m/s], which is determined by normal distribution with mathematical expectation \( V_g \) variance 1.

Thus, the velocity distributions of the sample gas particles for the X, Y and Z axes are demonstrated in Figure 4:

![Figure 4](image)

**Figure 4.** Normal particle velocity distribution along the Y, Z and X axes.

The separation of sample gas according to their chemical composition in a microfluidic gas chromatography column is implemented due to different impulse interaction of carrier gas and different probabilistic parameters of the sample gas components, namely, the probability of activation of adsorption processes.

Thus, the algorithms for the movement of the sample gas particles under the action of the carrier gas inside the microchannel and for the movement of the sample gas particles in the near-surface layer are based on the stochastic approach. Combining both algorithms into a single model allows creating of a tool for conducting numerical experiments at the stage of development of a microfluidic device to identify factors hindering its normal operation and further optimization of the device.

3. Modelling results

At the first stage of model development, the carrier gas velocity field was calculated in the “Laminar Flows” section of the Comsol Multiphysics 5.3 application program. This calculation is based on solving the differential Navier-Stokes equation. During the simulation, argon and helium were used as a carrier gas, the parameters of which were set from the built-in library of materials [12]. The pressure difference in the simulated area was calculated based on the assumption of a uniform pressure drop across the entire channel length of the microfluidic device with the following microchannel parameters: length 2.5 meters, the pressure difference between the inlet and outlet – \( 2 \times 10^5 \) Pa. The resulting velocity field corresponds to the laminar flow regime and is presented in Figure 5.

![Figure 5](image)

**Figure 5.** Example of the initial velocity field of a carrier gas.
As a result of the development in the Scilab 6.01.1 package, a comprehensive model of the processes of separation of the components of the gas mixture in a microfluidic gas chromatography column was obtained. In addition, visualization of physicochemical processes inside the channel was created (Figure 6). The geometric parameters of the channel are close to the size of some types of real microfluidic gas chromatographic columns: the column diameter is 14 $\mu$m.

The experiment was carried out at absolute temperature $T = 300$ K, the mass of particles of the carrier gas $m_c = 6.63 \times 10^{-26} \text{ kg}$, the mass of particles of the sample gas in this case was $m_p = 6.63 \times 10^{-26} \text{ kg}$, the diameter of particles of the sample gas $d = 1.4 \times 10^{-10} \text{ m}$, which corresponds to argon, number of particles $N = 1000$, probability of adsorption when a particle enters the cell near-surface layer $P_{ad} = 10\%$, probability of desorption after adsorption process $P_{des} = 4\%$. Simulation time is $t_{max} = 1 \times 10^{-7} \text{s}$. The diameter of the channel and its length, respectively, $D = 14 \times 10^{-6} \text{ m}$, $X = 1.5 \times 10^{-4} \text{ m}$.

The developed model takes into account adsorption processes, which clearly illustrates the distribution of particles along the coordinate along the channel (Figure 7).

![Figure 6. The appearance of the simulated system.](image)

![Figure 7. Histogram of the distribution of particles of a single-component sample gas along a spatial coordinate parallel to the axis of the channel.](image)
To demonstrate the process of separation of the sample gas inside the channel, a two-component mixture was selected, consisting of model gases A and B with different probabilistic parameters. An example of the gas mixture separation obtained during the simulation is shown in Figure 8.

**Figure 8.** The process of separation of the gas mixture into components A and B.

The experiment was carried out at absolute temperature $T = 300$ K. The parameters of particles A, which corresponds to helium, and B, which corresponds to radon, respectively:

1) $m_A = 6.64 \times 10^{-27} kg$, $d_A = 0.62 \times 10^{-10} m$, $N_A = 1000$, $P_{ad_A} = 10\%$, $P_{des_A} = 4\%$;
2) $m_B = 2.31 \times 10^{-25} kg$, $d_B = 1.84 \times 10^{-10} m$, $N_B = 1000$, $P_{ad_B} = 1\%$, $P_{des_B} = 0.5\%$.

Simulation time is $t_{max} = 1 \times 10^{-7}$ s. The diameter of the channel and its length, respectively, $D = 14 \times 10^{-6} m$, $X = 0.5 \times 10^{-4} m$. The average particle velocity of the carrier gas in the experiment is 5 m/s, which corresponds to the actual gas velocity in the microchannel. The spatial distribution of two-component sample gas particles along the channel axis is shown in Figure 9.

**Figure 9.** Histogram of the distribution of particles of a two-component sample gas along a spatial coordinate parallel to the axis of the channel.

The simulation result can be represented both in the spatial domain (in the form of a distribution of gas sample particles in the microchannel volume) and in the time domain (in the form of a
chromatogram). The results obtained are in qualitative agreement with the data known from the literature [10], which allows us to conclude that the proposed method can be used for the preliminary modelling of the operation of a microfluidic gas chromatographic column in order to solve the problem of optimizing the design of a microfluidic system and optimally select the analysis constructional-technological work.

4. Conclusion
As a result of the work performed, the following results were achieved:
- a methodology has been developed for modelling separation processes inside a microfluidic gas chromatographic column;
- on the basis of the proposed methodology, a model was created that simulates the operation of a microfluidic gas chromatographic column, which consists of transporting and separating the gas mixture into components that are subject to different effects of the sorbent;
- in the process of conducting numerical experiments, the spatial distribution of particles of a sample gas consisting of two components was obtained, demonstrating the presence of separation processes due to the different nature of the adsorption processes in the case of particles of different types.

The developed model takes into account such physicochemical processes as the adsorption and desorption of sample gas particles on the surface of the microchannel wall of the column and the probabilistic interaction of the sample gas particles and the carrier gas. In this paper, the description of the motion of the sample gas particles under the action of the carrier gas, the velocity field of which is calculated based on the Navier-Stokes equations, and the description of the particle behaviour in the surface layer, whose parameters are calculated using the molecular dynamics method, are based on the stochastic approach. In the process of carrying out numerical experiments, spatial distributions of particles of one- and two-component sample gas were obtained, demonstrating the presence of adsorption and separation processes inside a simulated microfluidic gas chromatographic column. Further investigation will be directed on the improvement of the model of the behaviour of particles in the near-surface layer.

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