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SIMULATION OF ADSORPTION AND DESORPTION PHENOMENA IN A GAS CHROMATOGRAPHY MICROCOLUMN

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ABSTRACT

The main goal of the present work is to optimize the micro-column for the gas chromatography analysis device, which is the device used in the real-time monitoring of atmospheric BTEX concentration for indoor environments. The BTEX group of molecules (Benzene, Toluene, Ethylbenzene and Xylenes) is, among volatile organic compounds (VOC), the most widely found in indoor air and its main sources are the cleaning products, building materials and outdoor air supply [1]. Among the BTEX compounds, Benzene is the most dangerous one, since it has been proven as a carcinogenic component [2]. The European Commission report [3] stated that the limit concentration of Benzene in an indoor environment should be $5\mu\text{g}/\text{m}^3$. Therefore, it is really important to measure the concentration of these species in indoor environments. The separation of BTEX takes place inside the micro-column is due to the adsorption and desorption phenomena. The relative rates of adsorption and desorption onto and off the stationary phase inside the chromatographic column allow chemicals in the analyzed samples to be separated and then quantified.

Aiming to have a good performance of chemical detection, it is always important to have well-separated analytes in the GC column, hence designing an efficient column is crucial to the success of the microchemical detection system [4]. Usually, the micro-columns used in gas-chromatographs are silica tubes of about 150 to 300 microns in diameter and about 20 meters long [5]. These columns have a thin stationary phase layer coated onto the walls of about $1\mu\text{m}$ thick. The different adsorption and desorption rates between the species to be separated with the stationary phase will generate different interactions between them, and each species will reach the outlet of the micro-column in a distinct instant. Placed after the micro-column, another component of the gas chromatography device, called detector, is accountable for measuring the concentration of each specie in tested air sample. The final output provided by the gas chromatograph analyzed in the present work is a graph containing the concentration of the BTEX compounds species in time, called chromatogram.

In a very long and narrow channel and under isothermal conditions, the pressure and density could change considerably between the inlet and outlet in the function of the applied end conditions. Therefore, the velocity of the flow in the outlet cross-section of the column is higher than the velocity nearby the inlet. Consequently, even though the flow velocity is much smaller than the sound speed, the compressibility effect and the flow velocity variation with the position have to be considered. The working conditions of our micro-column are: outlet pressure of 1atm and temperature of 65°C . Under these conditions, the mean free path of Nitrogen, the



carrier gas, is $0.076\mu\text{m}$. Therefore, the flow regime inside our micro-column is always in continuum flow regime, with $\text{Kn} < 0.0005$.

The carrier gas flows in a long capillary of the circular cross-section of a radius $R=0.09\text{mm}$ and the length $L=20\text{m}$. The inlet pressure and outlet pressure are fixed to be equal to $p_{\text{in}}=4\text{bar}$ and $p_{\text{out}}=1\text{bar}$. The volumetric gas flow rate is measured on the outlet section of the capillary and it is equal to $Q=2.5\text{ml/min}$. From this measurement the averaged over the tube cross-section flow velocity can be calculated and it is equal to $u_{\text{av}}=Q/A_c = 1.64\text{m/s}$, where is the capillary cross-section. Taking into account mentioned parameters the Reynolds number is of the order of 1.

Very small quantity of the molecules of the BTEX group, of the order of several ppb, is injected into the capillary through the injection loop. Due to very small quantity of the injected molecules their interaction could be neglected and only the transport of a BTEX molecule in the carrier gas flow could be considered and the diffusion of the BTEX molecules through carrier gas. For each BTEX molecule the retardation time is measured, *i.e.* the time between its injection at the tube inlet section and its detection at outlet cross section by the detector. This retardation time is much longer compared to the characteristic flow time, *i.e.* a time needed to a molecule to pass from the inlet section to the outlet section: $t_f=L/u_{\text{av}}$. Therefore the adsorption-desorption phenomena have to be taken into account.

We consider the flow of compressible gas through a capillary of the circular cross-section with radius R driven by a force due to a static pressure applied to the fluid. The compressible Navier-Stokes equations in cylindrical geometry with (r, x) variables are used to describe this flow. The third variable does not taken into account because of symmetry condition in φ direction. The viscosity coefficient at $T=65^\circ\text{C}$ is calculated taking into account the viscosity at the reference temperature ($T_{\text{ref}}=0^\circ\text{C}$) and a viscosity index (ω) [6].

The velocity of the carrier gas along the column can be assumed constant along the coordinate r , but it is considered to vary along the coordinate x , being calculated from Eq.(1):

$$u_{\text{avg}}(x) = -\frac{R^2}{8\mu} \frac{dp}{dx} \quad (1)$$

and the pressure gradient along the column is calculated from Eq.(2):

$$\frac{dp}{dx}(x) = -\frac{p_{\text{in}}(1-p_r^2)}{2L} \left(1 - \frac{x}{L}(1-p_r^2)\right)^{-1/2} \quad (2)$$

being $p_r = p_{\text{out}}/p_{\text{in}}$.

The implemented adsorption model is the largely used Langmuir adsorption isotherm [7].

Since we are interested in the transport of the pollution molecules of the BTEX group by the carrier gas flow, the main aim is to describe the variation of the species concentration along the column in order to evaluate the so called retardation factor. The description of the concentration of species along the column can be done by two different ways: using the simplified model, considering constant velocity and diffusion coefficient along the column, and using the complete model, where velocity of carrier gas and diffusion coefficient varies along the column because of the pressure gradient.

The simplified model is presented by Eq.(3):

$$\frac{\partial n}{\partial t} + u_{\text{av}} \frac{\partial n}{\partial x} = D \frac{\partial^2 n}{\partial x^2} \quad (3)$$

where n is a BTEX species number density, u_{av} is the average velocity of the carrier gas along the microcolumn, calculated here by the division between the volumetric flow rate (Q) and the cross section areal of the column (A_c), and D is the diffusion coefficient.

When the initial boundary condition is a Gaussian one, the solution has the following form:

$$n(x, t) = n_0 \frac{mL}{2\sqrt{\pi} \sqrt{a^2 L^2 + t D_{Rf}}} \exp\left(-\frac{(x - t u_{Rf})^2}{4(a^2 L^2 + t D_{Rf})}\right) \quad (4)$$

Here n_0 is the injected density, a is the thickness of the Gaussian injection function, m is the molecular mass, x is the coordinate along the column, u_{Rf} and D_{Rf} are the carrier gas velocity and the diffusion coefficient normalized by the retardation time Rf . The analytical solution can also be presented in the dimensionless form, in order to make easier the comparison

$$\bar{n}(\bar{x}, \bar{t}) = \frac{a}{\sqrt{a^2 + \alpha \bar{t}}} \exp\left(-\frac{(\bar{x} - \bar{t})^2}{4(a^2 + \alpha \bar{t})}\right) \quad (5)$$

where α is the inverse of Peclet number, which is function of velocity of carrier gas (u), length of the column (L) and diffusion coefficient (D):

$$\alpha = \frac{1}{Pe} = \frac{u_{av} L}{D} \quad (6)$$

We obtained so far some results of concentration for Benzene from this analytical solution varying different parameters, among them the average velocity of carrier gas (Fig.1) and the length of the column (Fig.2).

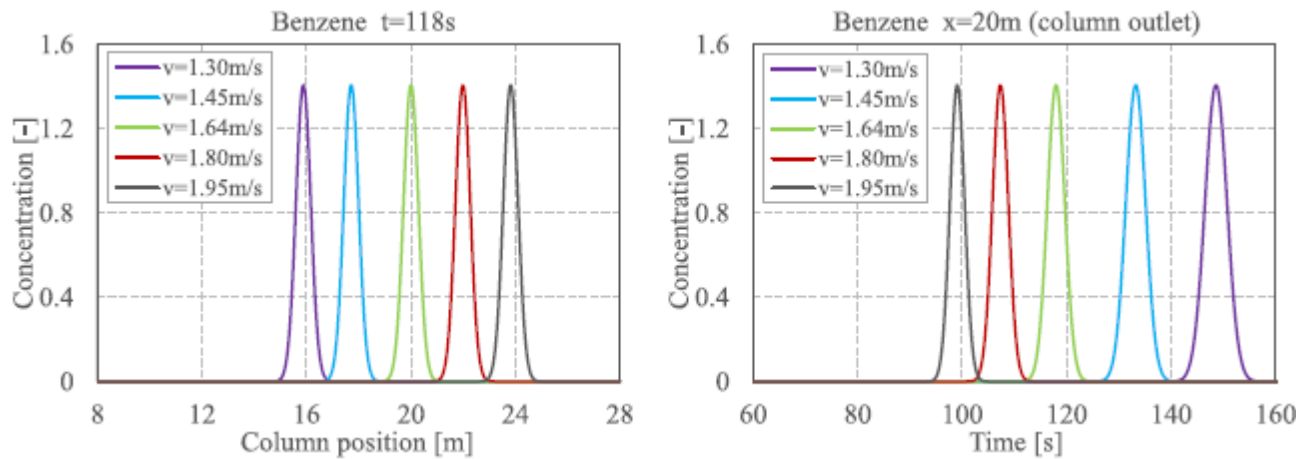


Figure 1: Concentration peaks for different velocities of carrier gas.

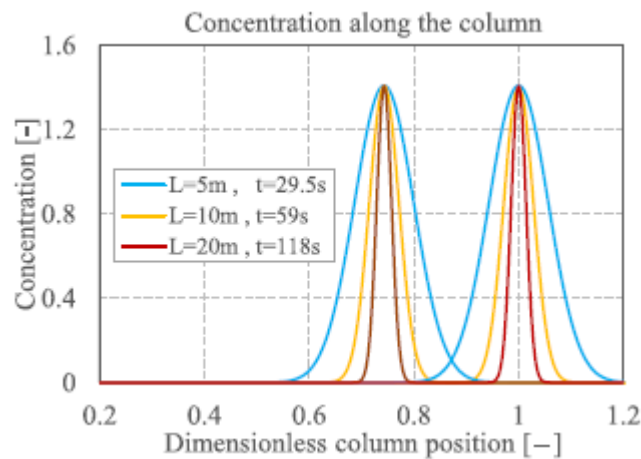


Figure 2: Concentration peaks for different microcolumn lengths.

From Fig.1, it can be concluded that increasing the velocity of the carrier gas impacts in a reduction of the time consumed to the Benzene reach the end of the micro-column. In other words, in order to reduce the time of the gas separation, it is necessary to increase the velocity of carrier gas. This can be done by increasing the pressure difference along the column.



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From Fig.2, it can be seen that decreasing the length of the microcolumn, the time consumed to the two quicker component reach the end of the micro-column is reduced as well. For instance, for $L=5\text{m}$ the time consumed is $t=29.5\text{s}$, while for $L=20\text{m}$, the time necessary is $t=118\text{s}$. However, for lower values of length, the resolution of the chromatogram is worst. This can be checked comparing the blue ($L=5\text{m}$) and red ($L=20\text{m}$) curves in the graph presented in Fig.2. The results in blue color show that the peaks of the two components are overlapping in a region, which presents an extra difficulty in accurately determining the exact quantity of each one of these two components. On the other hand, the results in red color show that the peaks are well apart from each other, which means that it is very easy to determine their exact quantity by integrating the area below the peaks.

The next step of the present work is to solve numerically the complete model. First, to take into account the variation of the carrier gas velocity and of the diffusion coefficient. Then, the advection-diffusion equation will be solved together with the adsorption-desorption fluxes balance equation.

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