Steady-State and Dynamic Systems for Diffusion Parameters Determination: Advantages and Disadvantages
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Steady-State and Dynamic Systems for Diffusion Parameters Determination: Advantages and Disadvantages

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Abstract

The counter-current gas diffusion measurements together with the chromatographic method in the single pellet string column (SPSC) configuration are discussed and compared. From both methods transport characteristics (parameters) of porous solids independent of measuring conditions can be evaluated according to the mean transport-pore (MTPM). The diffusion method is suitable for cylindrically shaped porous materials while the SPSC method allows measuring of peculiarly shaped porous materials, too. On the other hand, the diffusion method is suitable also for powder materials. The obtained transport characteristics from diffusion measurements and chromatographic method are compared.

Keywords: transport parameters, mass transport, Wicke-Kallenbach diffusion cell, Graham's diffusion cell, Single-Pellet String Column

1. Introduction

Two groups of methods (steady-state/dynamic) commonly used for pore-structure characterization (effective diffusion coefficients and transport parameters, $\langle r \rangle \psi$ and ψ) are discussed. Transport parameters are constants of the porous medium and play an irreplaceable role in modelling and design of chemical and biochemical processes (Petrissans et al.). Steady-state counter-current gas diffusion measurements in the Wicke-Kallenbach (Wicke & Kallenbach, 1941) and Graham's (Valuš & Schneider, 1981) diffusion cells and the dynamic chromatographic technique in the single-pellet string column configuration (SPSC) (Scott et al.) were used and the results compared.

2. Experimental

2.1. Gases

Four nonadsorbable gases — argon, nitrogen, helium and hydrogen (99.9 % purity, Technoplyn Linde, Czech Republic) were used both as carrier gases (mobile phase) and tracer gases.

2.2. Samples

Four porous materials with mono- and bidisperse pore structure were selected to cover a wide range of pore sizes. Textural properties determined by mercury porosimetry (AutoPore III, Micromeritics, USA) and helium pycnometry (AccuPyc 1330, Micromeritics, USA) are summarized in Table 1.

Sample	Most frequent pore radius[*)]	Porosity	Pore volume	Column void fraction
	[nm]	[–]	[cm^3/g]	[–]
ICI	10	0.465	0.302	0.491
G43-a	3.5/257	0.600	0.454	0.601
G4	46/630	0.525	0.279	0.651
G1	46/2330	0.579	0.348	0.633

Table 1: Textural properties of porous samples

Porosity was calculated from the apparent density (ρ_{Hg}) and true density (ρ_{He}) according to:

$$1 - \rho_{Hg}/\rho_{He}.$$
(1)

Column void fraction, α, in the chromatographic technique was evaluated from:

$$\alpha = \left(V_{col} - \frac{m_{pac}}{\rho_{Hg}} \right) \Big/ V_{col}$$
(2)

where V_{col} is column volume, m_{pac} is weight of samples and ρ_{Hg} is apparent density.

2.3. Experimental setup

Diffusion method

The isobaric counter-current diffusion measurements were performed in the experimental setup shown in Fig. 1 which permits to use both the Wicke-Kallenbach and the Graham technique. The diffusion cell was same for both experimental arrangements. It consists of two flow-through compartments separated by an impermeable disk with samples fixed in the cylindrical disc holes. For the classic Wicke-Kallenbach cell the outlet gas streams from both compartments were analyzed for the content of gases, whereas measurements in the Graham's diffusion cell was based on determination of the net volumetric diffusion flux by a digital bubble flowmeter (Optiflow 570, Agilent Technologies, USA) connected to the diffusion cell. During measurements the infinitesimal pressure differences between upper and lower cell compartments were registered by the differential pressure transducer (Baratron 600, MKS Instruments, USA). All measurements were performed at laboratory temperature and pressure.
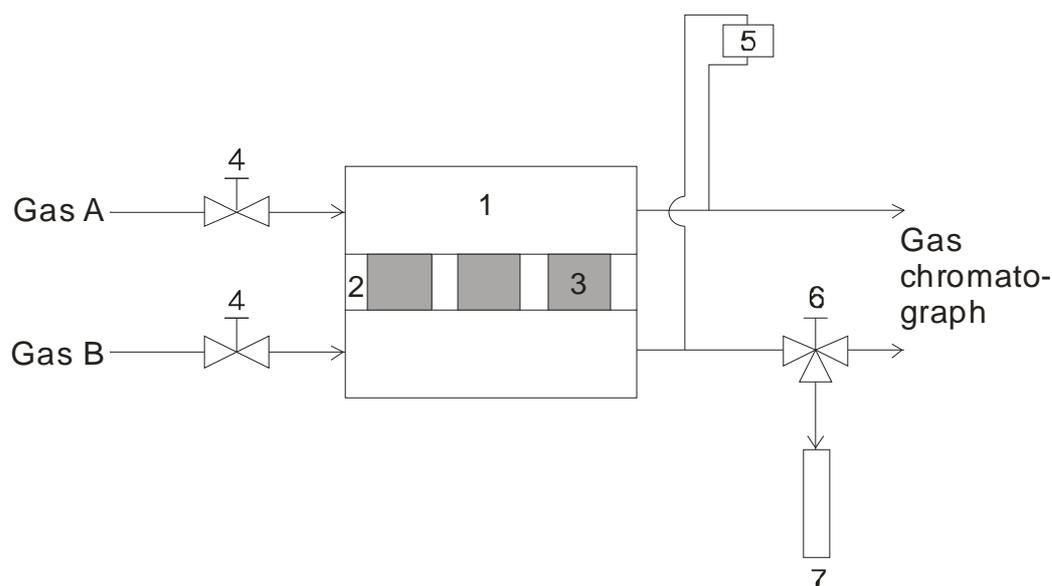
Figure 1: Diffusion setup. (1) – upper cell compartment, (2) – lower cell compartment, (3) – impermeable disk, (4) – porous pellets, (5) – valves, (6) – differential pressure transducer, (7) – three-way valve, (8) – digital bubble flowmeter

Chromatographic method

In SPSC configuration of the chromatographic column, particles are packed one by one into a column with diameter that exceeds only slightly (10–20 %) the particle dimension. A pulse of tracer gas is injected into the carrier-gas stream, which flows at constant flow rate through the column. The chromatographic apparatus is shown in Fig. 2. It consisted of chromatographic column, thermal conductivity detector (Micro-TCD, Gow-Mac Instruments Co., England), sampling loop (volume 273 μl) and calibrated mass flow-meters/controllers (Brooks Instument, Netherlands). Two stainless steel tubes (i.d. 0.8 cm, length 50 and 100 cm) were used as chromatographic column. All chromatographic measurements were performed at laboratory temperature and pressure.
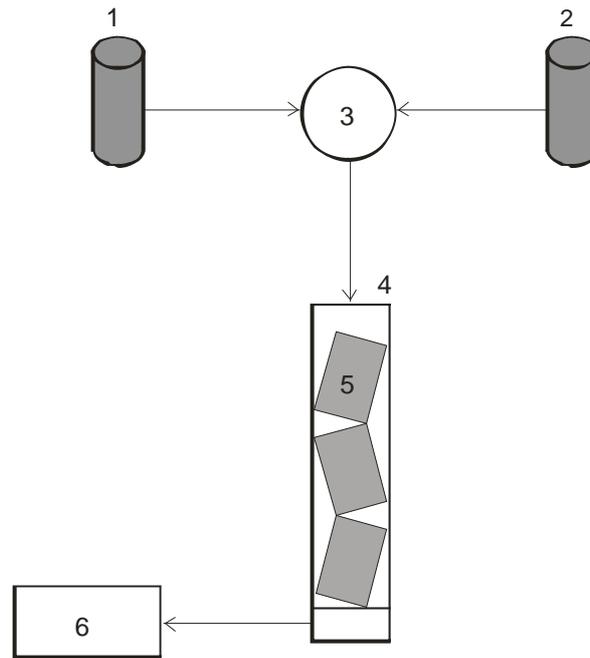
Figure 2: Chromatographic setup. (1) – carrier-gas source, (2) – tracer-gas source, (3) – six-way sampling valve, (4) – chromatographic column, (5) – porous samples, (6) – thermal-conductivity detector

3. Results and Discussion

Isobaric counter-current diffusion in porous solids was modelled by the Mean Transport-Pore Model (MTPM) (Schneider, 1978) which is based on the modified Maxwell-Stefan constitutive equation.

In the SPSC method, transport parameters were evaluated from response signals of column packed with porous samples. Analysis of outlet chromatographic peak was based on the Kubín-Kučera transport model (Kubín, 1965; Kučera, 1965). This model includes intracolumn processes, such as convection and axial dispersion of the tracer band, transport of the tracer through a laminar film around the porous particles, diffusion in the pore structure and adsorption (for adsorbable tracer gas) on the internal surface of porous packing. It does not account for processes upstream and downstream of the column (extra-column effects). It has been suggested (Šolcová & Schneider, 1996) to include these processes into the time-domain matching through application of the convolution theorem. This requires experimental system responses for two columns of different lengths (100 cm and 50 cm long columns were used in this work — see Fig. 3).
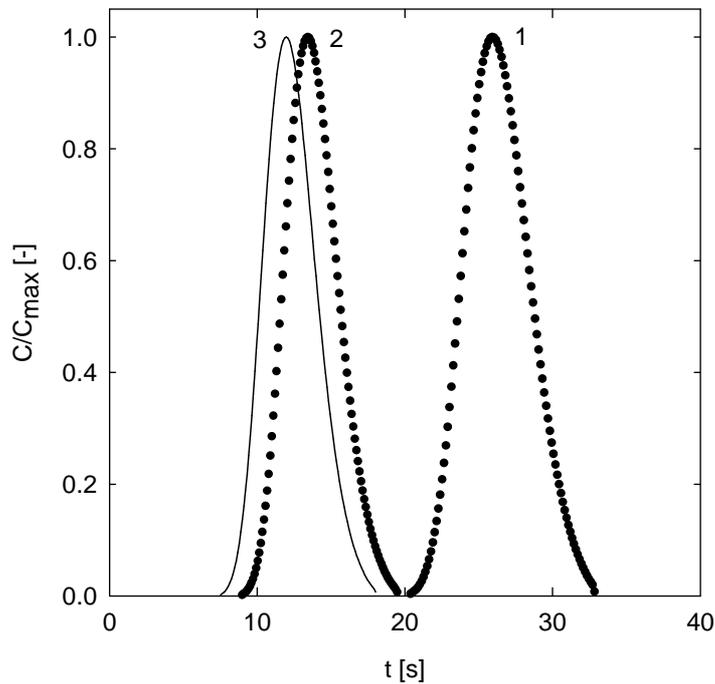
Figure 3: Column responses for G4 sample, He(mobile phase)/N_2(tracer). He volumetric flow 90 cm^3/min. (1) – column 100 cm, (2) – column 50 cm, (3) – calculated impulse response for 50 cm long column

3.1. Transport parameters evaluation

Transport parameters, $<r>\psi$ and ψ evaluated from diffusion measurements by nonlinear fitting of the set of experimental net molar diffusion flux densities obtained for different combinations and compositions of gases are summarized in the first part of Table 2. The mean transport pore radii, $<r>$, were computed from ($(<r>\psi)/\psi$).

Effective diffusion coefficients from chromatographic measurements (including transport parameters) were calculated from diffusion times obtained by time-domain fitting of the corresponding column responses. The obtained transport parameters, $<r>\psi$ and ψ, for all samples are summarized in the second part of Table 2.

It can be seen from Table 2 that for all samples the mean transport pore radii are in a good agreement. Differences between parameters ψ (which is defined as the ratio of transport pore porosity to transport pore tortuosity) could be explained by the different diffusion path-length (tortuosity) under steady-state and dynamic conditions.

Sample	Diffusion			SPSC		
	<r>ψ [nm]	ψ [–]	<r> [nm]	<r>ψ [nm]	ψ [–]	<r> [nm]
ICI	2.7	0.037	73	2.27	0.027	84
G43-a	7.8	0.031	252	1.95	0.013	302
G4	60	0.09	663	18	0.034	526
G1	153	0.19	803	47	0.055	861

Table 2: Transport parameters from diffusion measurements and SPSC method

4. Conclusions

On a set of four porous samples it was confirmed that consistent transport parameters can be obtained both by the steady-state method (counter-current gas diffusion) and diffusion measurements under dynamic conditions (SPSC method). The main advantage of the SPSC chromatographic method is that it enables determination of transport parameters for variously shaped porous materials (asterisks, asterisks with holes, lenses, extrudates, washcoats, etc.), while the diffusion cell methods requires cylindrically shaped pellets only. Another advantage of the SPSC is the averaging of obtained transport parameters over many pellets (usually hundreds of pellets as compared with several pellets in the diffusion cell). On the other hand, in steady-state diffusion measurements with nonadsorbable gases only diffusion transport process takes place, while in the chromatographic column other processes, such as convection and axial dispersion and transport of the tracer through a laminar film around solid particles have to be taken into account.

Acknowledgement

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