NATURAL CONVECTION IN CHROMATOGRAPHIC COLUMNS

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Natural convection in a granular bed is generally caused by a high-density gradient in the gaseous or liquid medium that fills the bed[1]. Convection currents in a granular bed filled with a gas and heated either from below or from one side and also a strong influence of such convection on the effective thermal conductivity have been observed. It has been shown that convection currents are also caused by the dissolution of the granular bed material in the liquid that flows through the bed. It has recently been observed that natural convection has an appreciable effect on heat-exchange processes in granular beds[2] and in totally or partially closed cavities[3].

The generation of convection currents in a granular bed is determined by the following modified criterion[4]:

$$\left(Ar_{gr} \cdot \frac{Sc \cdot h^2}{d_{eff}^2} \cdot \varepsilon \right)_{crit.} \geqq 700 \qquad (1)$$

where

$$Ar_{gr} = \frac{gd^3}{v^2} \cdot \frac{\varepsilon^3}{(1-\varepsilon)^3} \cdot \frac{\gamma^x - \gamma}{\gamma} = \text{Archimedes criterion} \qquad (2)$$

$Sc = v/D_G$ = Schmidt criterion
$d_{eff} = 4\varepsilon/a$ = effective diameter of the granular bed
d = grain diameter
a = the surface area of a granular bed volume unit
ε = bed voidage
h = the height of the bed in which convection current may occur
g = 9.8 m/sec
v = kinematic viscosity
D_G = diffusion coefficient
γ = average specific gravity of the gas (or liquid)
γ^x = specific gravity of the gaseous (or liquid) bed of a higher or lower density.

Considerable concentration gradients, as well as gas-flow specific gravity gradients in gas chromatography when the carrier gas and the eluting component have different specific gravities, led us to look for natural convection phenomena in chromatographic columns. Small packing grain diameters that reduce convection currents may be compensated by a substantial value of $\gamma^x - \gamma$ and by high ratios of h/d_{eff}. Natural convection must cause the component volume in the chromatographic peak zone to acquire a velocity of its own with respect to the carrier gas stream in a vertical column. Consequently, if $\gamma^x > \gamma$, the retention time t_2 for the upward carrier gas flow must be greater than the corresponding value t_1 for the downward gas flow. In all instances, additional peak spreading should be expected.

TABLE I

RETENTION TIMES (sec) AND PEAK HALF-WIDTHS FOR DOWNWARD (t_1, μ_1) AND UPWARD (t_2, μ_2) CARRIER GAS FLOWS THROUGH THE COLUMN

Component	Nitrogen							Helium						
	t_1	σ	t_2	σ	Δt	μ_1	μ_2	t_1	σ	t_2	σ	Δt	μ_1	μ_2
Methane	38.35	0.1	38.22	0.1	-0.13	5.3	5.1	39.5	0.1	39.5	0.1	0.3	5.4	5.8
Air	41.20	0.1	41.21	0.1	0.01	6.0	6.0	39.2	0.1	39.6	0.1	0.4	5.5	5.9
Ethylene	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hexane	131.0	0.8	133.0	1.0	2.0	15.6	18.0	141.0	2.3	145.0	2.4	4.0	15.8	18.8
Octane	500.0	7.0	578.0	8.0	12.0	30.0	40.8	630.0	5.0	655.0	6.0	25.0	33.6	39.0
Nonane	1270.0	20.0	1397.0	20.0	31.0	70.2	81.0	1374.0	17.0	1434.0	15.0	60.0	66.1	72.0

TABLE II

RETENTION TIMES (min) AND PEAK HALF-WIDTHS FOR UPWARD (t_1, μ_1) AND DOWNWARD (t_2, μ_2) FLOWS IN THE COILED SECTION OF THE COLUMN

Test conditions: Perkin-Elmer Model 451 chromatograph. Coiled column, 8 m long, 4 mm I.D., packed with 0.2–0.3 mm grain diameter Spherochrome-2 containing 20% of benzyl benzoate. Temperature 60°; carrier gas flow-rate 50 ml/min.

Component	Argon					Nitrogen					Helium				
	t_1	t_2	Δt	μ_1	μ_2	t_1	t_2	Δt	μ_1	μ_2	t_1	t_2	Δt	μ_1	μ_2
Methane	3.37	3.36	-0.01	—	—	3.36	3.35	0.01	—	—	3.56	3.57	0.01	—	—
Propane	4.42	4.43	0.01	—	—	—	—	—	—	—	—	—	—	—	—
Butane	6.68	6.70	0.05	—	—	—	—	—	—	—	—	—	—	—	—
Pentane	12.64	12.70	0.06	0.38	0.40	10.60	10.62	0.02	0.32	0.36	11.52	11.60	0.08	0.32	0.34
Hexane	28.00	28.15	0.15	0.86	0.90	21.68	21.80	0.12	0.65	0.74	23.61	24.00	0.39	0.68	0.72
Heptane	67.44	67.85	0.41	2.08	2.16	—	—	—	—	—	—	—	—	—	—

Elution characteristics were measured on a specially designed chromatograph with a thermal conductivity detector in order to detect the natural convection effect. The experiments were carried out under conditions that excluded all possible changes in retention time, caused by a difference in the values of dead space, sample volume, carrier gas velocity, etc. The column used was a vertically mounted tube, I m long and 4 mm I.D., packed with 0.3–0.4 mm grain diameter Spherochrom-2 containing 20 % of bis-2-methoxyethyl adipate. The column was conditioned at 30° with a temperature tolerance of not more than 0.10°. The temperature gradient of the conditioning liquid along the column did not exceed 0.10°. The carrier gas flow-rate was maintained at 20 ml/min, accurate to within 1 %. The samples were injected with a syringe directly into the packing through a sealed inlet.

At equal sample volumes, the average weight concentrations of the components in the peak zone were 10–1 % for nitrogen and 40–8 % for helium. The direction of the eluting component flow was changed by introducing the component into the column either from below or from above. At the same time, the positions of the sample inlet and the detector were altered by turning the whole assembly through 180°. Thus in each set of runs, identical hydrodynamic conditions of the component zone flow through the column in both directions were obtained.

The results of the measurements of elution parameters for two carrier gases, nitrogen and helium, with different masses, M_G, are given in Table I. The retention times for C_1–C_9 hydrocarbons and air, and the half-widths, μ, are average values of ten replicate tests. The standard deviations, σ, for the retention times t_1 and t_2 are calculated from the formula:

$$\sigma = \sqrt{\frac{\varepsilon(t_i - \bar{t})^2}{n - 1}}$$

where t_i is the retention time, i the serial number of the measurement, $\bar{t}$ the arithmetic mean retention time and n the number of measurements.

The tabulated results show the manner in which the residence times of the components in the column depend on the direction of their vertical movement, which is changed by the carrier gas. When the sample is introduced from above, all compounds whose specific gravities are greater than that of helium or nitrogen emerge faster from the column. In the methane–nitrogen system, the component to be eluted is lighter than the carrier gas. Here, the force of gravity acts in a direction opposite to that of the carrier gas flow. As a result, methane emerges earlier when it is introduced into the column from below. The absolute values of the retention time shifts, $\Delta t = t_2 - t_1$, caused by changing the direction of the sample injection and carrier gas flow, are greater than the standard deviation for each average t_1 and t_2. In one instance only, when the masses of the eluting ethylene and of the carrier gas were essentially the same, was the difference in retention times within the required accuracy of measurement.

In all the experiments, except for the elution of ethylene with nitrogen, the criterion value calculated from eqn. 1 was much greater than the critical value, thus permitting natural convection to develop in the granular bed of the column.

Fig. 1 shows relative differences in retention times, $\Delta\tau = \Delta t/[(t_1 + t_2)/2]$, as functions of differences in molecular weights of the eluting component and of
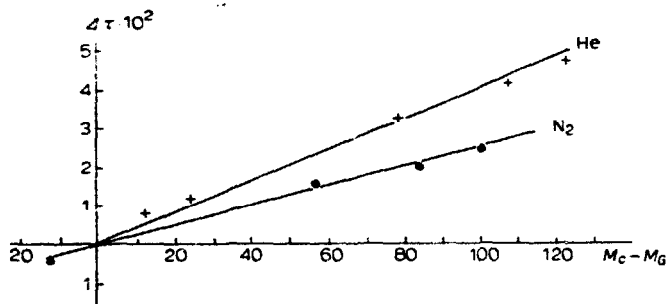
Fig. 1. Relative differences in retention times ($\Delta\tau$) as functions of differences in molecular weights of the eluting component and of the carrier gas ($M_C - M_G$).

the carrier gas ($M_C - M_G$). A linear dependence of $\Delta\tau$ on $M_C - M_G$ is apparent both for the light and the heavy carrier gases (helium and nitrogen).

The effect of natural convection on retention times is also observed in columns with different lengths of the ascending and descending sections of the packing (*e.g.*, in an 8-m coiled tube) (Table II). The residence time of components in the coiled section of the column is one order of magnitude greater than that in its vertical section. Therefore, when $M_C > M_G$, the retention time of the eluting component was always greater when the carrier gas in the coiled section of the column moved upwards. This also caused a peak-broadening effect (Tables I and II).

It will be noted that for heavier components the peak half-width, μ, is always much greater when the eluting component moves upwards, *i.e.*, against the force of gravity. Hence, natural convection may be one of the factors that causes hydro-dynamic mixing phenomena in a granular bed[5,6] and the broadening of a chromato-graphic peak.

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