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Note

A chromathermographic method for the determination of adsorption isotherms at high adsorbate concentrations

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Zhukhovitskii and co-workers^{1,2} described a method for the determination of adsorption isotherms based on the theory of chromathermography at low concentrations. In recent years, gas chromatography at high concentrations (the so-called "chromatography without carrier gas", CWCG) has been developed³, and the theory of processes in equilibrium CWCG with a moving temperature field (CTWCG) has been discussed^{4,5}. The possibility of using CTWCG for analytical purposes has also been considered⁶.

This paper is devoted to the development of the previous method for measuring isotherms by CTWCG. The concentration distribution at equilibrium is described by the following equations:

$$-\frac{\partial(\alpha N_1)}{\partial x} = \frac{\partial a_1}{\partial t} \quad (1)$$

$$-\frac{\partial(\alpha N_2)}{\partial x} = \frac{\partial a_2}{\partial t} \quad (2)$$

where N_1 and N_2 are the concentrations of the main component and the carrier gas, respectively, a_1 and a_2 are the adsorption values of these components for unit volume of the sorbent bed, α is the flow-rate, x is the axial distance from the column inlet, and t is time. As shown previously^{4,5}, the movement of an oven with a variable temperature field along the column leads to a broadening of the zones characteristic of CTWCG, and simultaneously to a narrowing of the zones due to the effect of the temperature field. The action of these two processes results in a stationary distribution of concentration on the sorbent bed. It is therefore possible to simplify the solution of eqns. 1 and 2 by introducing the coordinate $\psi = x - wt$, where w is the velocity of the temperature field. The system of usual differential equations obtained can be integrated, as a result of which the following expressions are obtained:

$$\alpha N_1 = a_1 w + C_1 \quad (3)$$

$$\alpha N_2 = a_2 w + C_2 \quad (4)$$

where C_1 and C_2 are integration constants. At $N_1 + N_2 = 1$, eqns. 3 and 4 give an expression relating α and a for any section of the column:

$$\alpha = w(a_1 + a_2) + C_1 + C_2 \quad (5)$$

The values of the integration constants can be determined from the boundary conditions near the characteristic temperature T_{ch} , which correspond to chromatography at low concentrations:

$$N_1 = 0 \quad (6)$$

$$N_2 = 1 \quad (7)$$

$$\alpha = \alpha_{ch} = \alpha_0 \cdot \frac{T_{ch}}{T_0} \quad (8)$$

where α_0 is the flow-rate at room temperature, T_0 . Let us suppose that the carrier gas is sorbed according to the linear equation

$$a_2 = \Gamma_2 N_2' \quad (9)$$

where Γ_2 is the Henry coefficient. Then, using eqns. 3, 4, 6, 7 and 8 we have $C_1 = 0$ and $C_2 = \alpha_{ch} - w\Gamma_2$. Elimination of α from eqns. 3-5 leads to a thermal equation of adsorption for CTWCG:

$$a_1 = \frac{\alpha_{ch} N_1}{w(1-N_1)} + (a_2 - \Gamma_2) \frac{N_1}{1-N_1} \quad (10)$$

As the second term in this equation, corresponding to the carrier gas adsorption, is usually much smaller than the first term, it can be neglected.

The isotherms were measured as follows. The values of α_0 , w and the amount of sample introduced were varied, and the elution curve and temperature of the bed at the end of the column were measured. Typical chromatograms of *n*-pentane on silica gel are shown in Fig. 1. The broken line corresponds to the temperature field of the oven. In order to calculate the value of adsorption (a_1), a number of vertical sections corresponding to different temperatures were drawn. The points of intersection of the vertical lines in Fig. 1 with the experimental curves determine the concentrations N_1 which were used in eqn. 10 to calculate a_1 . Only the points situated on the left-hand portions of the curves were used as the effect of diffusion can be neglected in this region. Using the sections of curves at different temperatures, a number of iso-

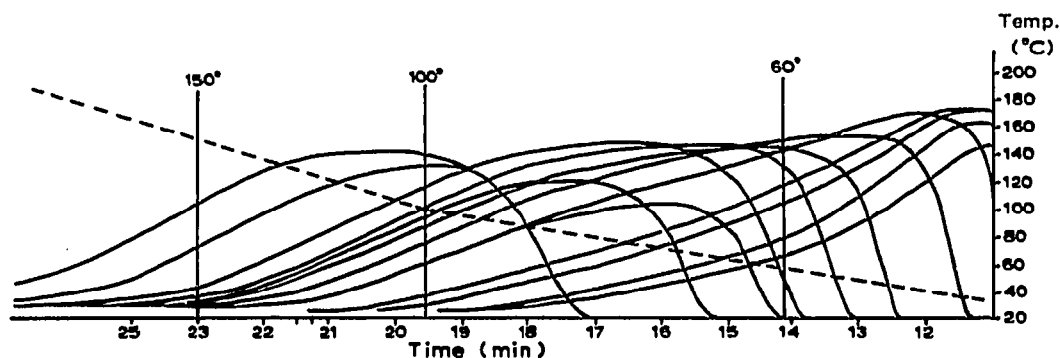


Fig. 1. Chromatograms of *n*-pentane at different values of α_0 . $w = 4.52$ cm/min. Column, 155 cm \times 0.4 cm (I.D.).

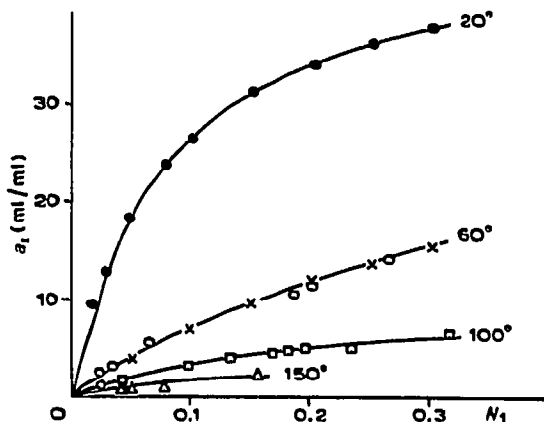


Fig. 2. Isotherms of *n*-pentane on silica gel (MCM grade). \times , \square , \triangle = CTWCG; \bullet , \circ = diffuse front desorption method.

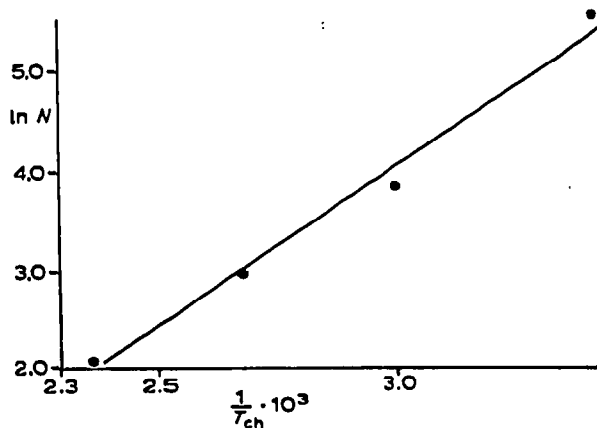


Fig. 3. Plot of $\ln N_1$ against $1/T_{ch}$.

therms can be obtained. Fig. 2 shows the isotherms of *n*-pentane on silica gel (MCM grade) obtained by the method described above. For comparison, experimental points for isotherms at 20° and 60° obtained by the diffuse front desorption method⁷ are also shown. From the isotherms obtained, the heat of adsorption of *n*-pentane on silica gel (at $a_1 = 2$ ml/ml) (Fig. 3) was calculated to be approximately 6.5 kcal/mole.

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