STATIONARY PHASE DISTRIBUTION IN OPEN TUBULAR GLASS COLUMNS

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The distribution of a stationary phase in open tubular glass columns was studied from photographs of their inner surface. It was reestablished that the stationary liquid phase is present in the column in the form of a dense network of small droplets. It was found by measuring the size of the droplets in columns with different quantity of the stationary phase that the size of the droplets is always the same and does not depend on the phase quantity. The phase quantity in the column calculated from the density of the droplets is in good agreement with that found by weighing. The phase distribution in the column influences the relative heats of solution and the retention indexes.

The efficiency of open tubular columns depends on the distribution of the stationary phase on the column walls. The views on the mode of the phase distribution in the columns are different. In efficient open tubular columns, the phase should be distributed in the form of a thin homogeneous film[1]. However, Giddings[2] pointed out the impossibility of the formation of a homogeneous film. In the case of a film formation, the liquid phase would accumulate more or less rapidly according to its viscosity in the place of the smallest diameter. Every change of the capillary diameter would thus cause accumulation of the stationary phase and eventually choking of the column. To eliminate this obstacle, variations of the capillary diameter should be smaller than about $\pm 5\%$, which cannot be achieved in practice. Since no such accumulation of the liquid was observed, we can deduce that the stationary phase is present on the capillary walls in the form of a network of tiny droplets. This concept is supported by electron microscopic studies of the capillary surface[3]. It was also observed that with columns containing different volumes of the stationary phase the mass transfer resistance in the liquid phase changes only little. This could be explained on the assumption that the droplet diameter is constant and only their number varies.

It follows that the meaning of the film thickness introduced in gas–liquid chromatography is problematical. The film thickness in neither a measure of the column efficiency nor of the wetting homogeneity. We observed that columns with an equal thickness of the stationary phase film differ considerably in their efficiency, and we attempted in this work to elucidate certain questions related to the phase distribution in open tubular columns, a problem which has been of interest during the last time.

EXPERIMENTAL

Chemicals and Apparatus

Stationary phase: OV-101 (Applied Science Laboratory, State College PA, U.S.A.) Substances: n-pentane. n-hexane, n-heptane, n-octane, 3-methylpentane, 2,3,4-trimethylpentane, 2,3-dimethylhexane, 3-methylheptane, 2,2,5-trimethylhexane (A.I.P. Standards, State College, PA, U.S.A.), benzene of reagent grade (Lachema, Brno), and methyltrifluorochlorethyl ether (Institute of Chemical Technology, Prague).

Gas chromatographic analyses were made on the previously described apparatus[4]. Glas columns were manufactured in a similar way as described by Desty[5], etched by methyltrifluorochlorethyl ether vapour[6] and coated with the stationary phase OV-101 by the dynamic method. A 5% solution of the OV-101 in benzene was used at different flow rates according to the desired thickness of the stationary phase film[7]. The column was connected with a open tubular column ($L = 20$ m) to keep the flow rate of the wetting solution constant. After the coating, the columns were stabilized at 80° C during passage of nitrogen for 3 days. The amount of the deposited phase was determined from the weight increment as well as by washing the column with a solvent, evaporating and weighing the residue. The columns were tested at 50°C on using n-heptane; their parameters are given in Table I.

Photographing. The inner surface of the open tubular columns was photographed with the use of a microscope type DRU 3 with a photographic equipment (Meopta, Prague).

Measurement of the contact angle. The contact angle was determined by measuring the meniscus directly in the open tubular column with a microscope (magnification 50×) or after projecting the image of the meniscus on a projection screen.

RESULTS AND DISCUSSION

It follows by comparing the optimum parameters of the open tubular columns (Table I) that their efficiency varies widely although all columns were prepared in the same way. Most efficient is the column H with the largest mean film thickness.
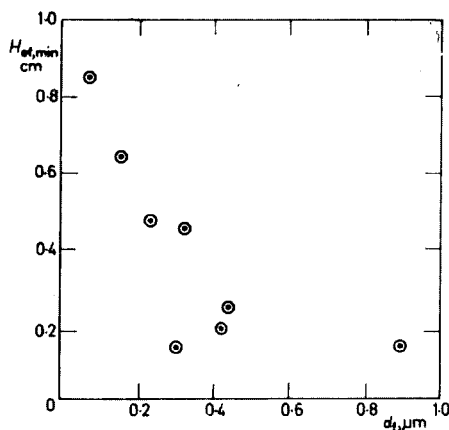
FIG. 1

Dependence of Relative Broadening of the Peak, $H_{min,ef}$, on Mean Stationary Phase Film, Thickness d_f

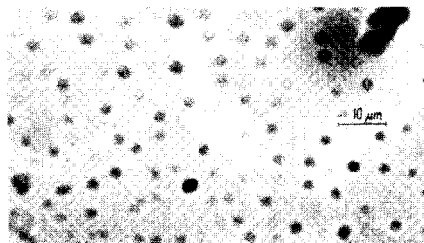Measured at 50°C; n-heptane on OV-101; columns from Table I.

Fig. 2

Internal Surface of Coated Open Tubular Column

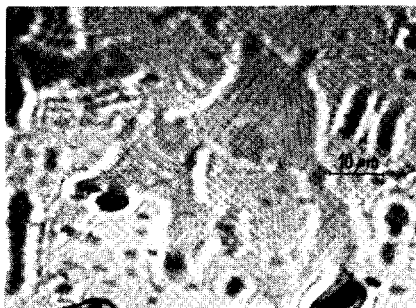Column A from Table I, magnification $1 : 6 \cdot 6 . 10^{-4}$.

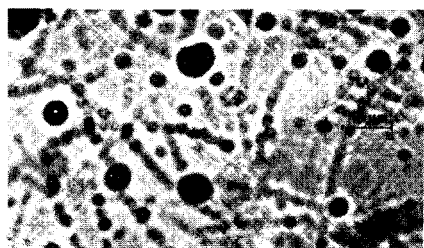Fig. 3

Freshly Prepared Open Tubular Column H

Fig. 4

Column H after 24 h Conditioning under Nitrogen at 80°C
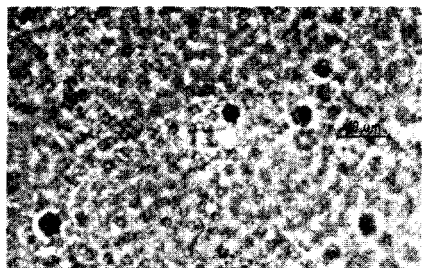

Fig. 5

Column H after 3 Days Conditioning under Nitrogen at 80°C

Also the column F is efficient, where in the only case the internal surface was not etched. The column A with the least amount of the stationary phase is least efficient. It is obvious that the efficiency depends on the phase content but this dependence is not unambiguous. According to the Golay equation, H_{min} should increase with d_f^2, hence the most efficient columns should have the thinnest film. However, thin films are easily ruptured and the phase is not evenly distributed. According to our measurements, in the case of the stationary phase OV-101 and with n-heptane, the value of $H_{min,ef}$ decreased with d_f (Fig. 1).

In view of the irreproducibility of the preparation of open tubular columns and different opinions as to the distribution of the stationary phase in them, we studied this problem in more detail. The observation of the internal surface showed conclusively that the stationary phase is distributed evenly in the form of a network of tiny droplets; a typical example is shown in Fig. 2.*

We assume that during coating the column by the dynamic method the stationary phase solution adheres first on the inner capillary walls in the form of a thin film. During evaporation of the solvent, this film gradually disintegrates to form "pools", then "chains" and eventually a regular network of droplets of the stationary phase. As an illustration, Fig. 3* shows the freshly coated column H, where the disintegration of the stationary phase film to pools is visible; Fig. 4* shows the chains of the stationary phase in the same column after 24 h stabilization during passage of nitrogen at

TABLE I

Parameters of the Columns Used

Column	Length m	Inner diam. mm	Phase quantity g	Film thickness μm	$H_{min,ef}$ cm	u_{min} cm/s	Rel. reten. $r_{c6/c7}$	Capacity ratio k
A	34·6	0·25	0·0028	0·08	0·85	18·5	2·23	0·56
B	22·0	0·24	0·0022	0·15	—	—	—	—
C	22·0	0·24	0·0037	0·23	0·48	25·9	2·46	0·81
D	22·0	0·24	0·0042	0·29	0·15	10·4	2·43	0·94
E	22·0	0·24	0·0050	0·31	0·46	12·7	2·35	0·84
F^a	20·7	0·50	0·0129	0·41	0·17	41·2	2·54	0·43
G	22·0	0·24	0·0070	0·43	0·24	16·2	2·39	1·15
H	22·0	0·24	0·0143	0·88	0·14	15·5	2·43	2·63
I^b	20·0	0·26	0·0010	0·06	—	—	—	—

[a] The internal surface was not etched. [b] The column was coated with the stationary phase by the static method, others by the dynamic method.

80°C; only after a three-day stabilization the phase distribution in the column became homogeneous (Fig. 5*).

We attempted to determine the size of the droplets from the mentioned photographs for the columns A, F, G and I differing by their phase quantity. We calculated the normal distribution of the droplet diameter, a, from 30 measured values according to the equation

$$\varphi(a) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(- \frac{(a - \bar{a})^2}{2\sigma^2} \right), \tag{1}$$

TABLE II

Comparison of the Calculated Phase Quantity in the Column with that Found by Weighing

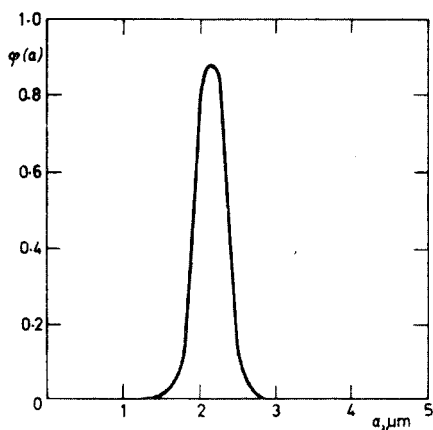| Column	Phase quantity found by	
	weighing	calculation
A	0·0028	0·0109
F	0·0129	0·0119
G	0·0070	0·0054
I	0·0010	0·0009

FIG. 6

Normal Distribution of Droplet Diameters Columns A, F, G and I from Table I.
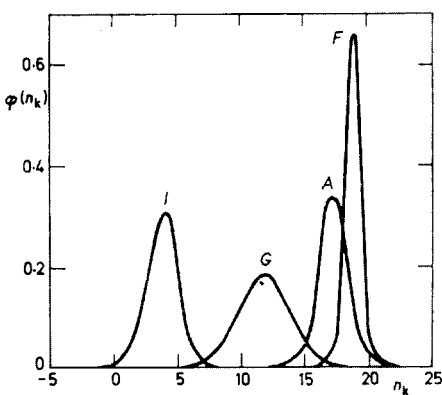

FIG. 7

Normal Distribution of the Number of Droplets per 100 μm^2
Columns A, F, G and I from Table I.

*See insert facing page 520.

where $\bar{a}$ denotes mean droplet diameter and σ standard deviation (Fig. 6). The value corresponding to the maximum frequency was determined as $a = 2\cdot1$ μm. It is seen from Fig. 6 that the droplet diameter is approximately constant in all the mentioned columns and independent of the phase quantity. The droplet volume, $V_k = 3\cdot0$ μm^3, was calculated from its diameter, a, and the contact angle, $\vartheta = 23 \pm 0\cdot5°$, according to the formula

$$V_k = \frac{a^3}{24} \frac{(1 - \cos \vartheta)(2 + \cos \vartheta)}{\sin \vartheta (1 + \cos \vartheta)} .$$

(2)

The number of droplets per unit area was also determined for the columns A, F, G and I; the normal distribution is shown in Fig. 7. The total mass of the stationary phase in the column, m, can be found from the volume of one droplet, V_k, its density, ϱ, radius and length of the capillary, r and L, and number of droplets per unit area, n_k, as follows:

$$w = 2\pi r L V_k \varrho n_k / 100 .$$

(3)

The calculated amounts (Table II) are in good agreement with those found by weighing except for the column A.

The phase distribution along the column was studied with columns A and F, which were divided into four and three parts, respectively. The capacity ratio, $k = t_R/t_M - 1$, was measured for the different parts (Fig. 8) and the average number of droplets per
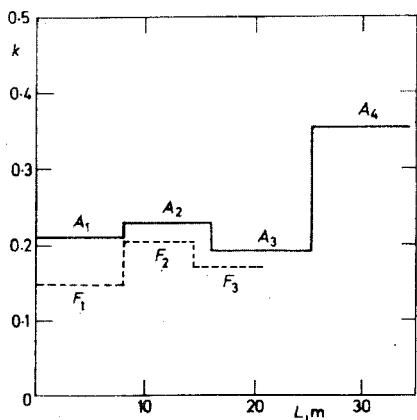

FIG. 8

Division of Columns A and F into Sections and the Corresponding Measured Capacity Ratios k
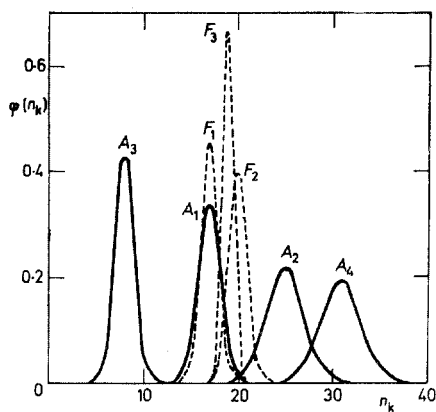

FIG. 9

Normal Distribution of the Number of Droplets per 100 μm^2 in Different Sections of the Columns A and F

TABLE III

Dependence of Relative Heats of Solution $\Delta H_{s(rel)}$ on the Stationary Phase Quantity in the Column

Compound	$\Delta H_{s(rel)}$, kcal mol^{-1}			
	B (0·15 μm)	C (0·23 μm)	D (0·29 μm)	H (0·88 μm)
n-Pentane	+1·66	+2·16	+2·22	+1·99
Cyclopentane	+1·12	+1·62	+1·79	+1·65
n-Hexane	+0·70	+1·02	+1·24	+0·99
Benzene	+0·66	+0·94	+0·88	+0·84
n-Heptane	0·00	0·00	0·00	0·00
2,3,4-Trimethylpentane	−0·29	−0·28	−0·25	−0·28
2,2,5-Trimethylhexane	−0·47	−0·75	−0·85	−0·81
n-Octane	−0·71	−0·96	−1·02	−1·05

TABLE IV

Influence of the Amount of the Stationary Phase on the Magnitude and Precision of the Retention Indexes ($t = 50°$C)

Compound	B (0·15 μm)		C (0·23 μm)		D (0·29 μm)		E (0·31 μm)		H (0·88 μm)	
	I	σ	I	σ	I	σ	I	σ	I	σ
Cyclopentane	564·55	0·84	565·34	0·82	—	—	566·45	0·17	565·91	0·18
3-Methylpentane	582·06	0·61	—	—	583·89	0·14	583·58	0·11	583·91	0·09
Benzene	654·97	0·45	654·59	0·51	652·61	0·23	653·55	0·34	652·11	0·17
2,3,4-Trimethyl-pentane	748·64	0·16	749·43	0·13	750·27	0·05	750·34	0·21	750·39	0·09
2,3-Dimethylhexane	759·27	0·22	760·57	0·28	760·51	0·06	760·57	0·05	760·83	0·10
3-Methylheptane	772·69	0·28	773·00	0·15	773·91	0·14	773·72	0·14	773·97	0·11
2,2,5-Trimethyl-hexane	782·69	0·29	783·95	0·15	784·09	0·48	784·22	0·22	784·63	0·14

unit area, n_k, was determined. The droplet distribution in the individual column sections is shown in Fig. 9. In the column F, the stationary phase is spread homogeneously on the capillary walls as can be seen from Fig. 8 (small changes of the capacity ratio along the column) and Fig. 9. The efficiency of this column is relatively high. With the column A, Figs 8 and 9 show an inhomogeneous distribution of the stationary phase. On some places the column was practically uncoated; this circumstance influenced considerably its efficiency and caused disagreement of the values in Table II. The phase distribution in the column influences also the relative heats of solution and retention indexes. The relative heats of solution, $\Delta H_{s(rel)} = \Delta H_{s(sorb)} -$ $- \Delta H_{s(hept)}$, given in Table III should be constant for all sorbates on columns differing only by the phase quantity. Small differences in $\Delta H_{s(rel)}$ are an evidence for a homogeneous coating of the columns C, H and O. Larger differences, especially with benzene on the column B, can be attributed to adsorption on uncoated sites of the capillary column.

The influence of the stationary phase on the retention indexes was studied with one glass open tubular column which was gradually coated with the stationary phase; after finishing the work the phase was removed with a solvent and the mean film thickness calculated. In this way, the columns B, C, D, E and H with different phase quantity were prepared and their retention indexes at 50°C for some hydrocarbons measured (Table IV). It is obvious that the retention indexes depend slightly on the phase quantity in the column. This dependence is most pronounced in the case of benzene, where the retention index decreases with increasing coating since the adsorption on the surface decreases. In contrast, with nonpolar hydrocarbons the retention indexes increase with the coating since the solubility increases. The retention indexes for $d_f = 0.29, 0.31$ and 0.88 μm are practically identical, an evidence for a homogeneous coating of the inner surface of the column.

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