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# FLOW CHARACTERISTICS AND TECHNOLOGY OF CAPILLARY COLUMNS WITH INNER DIAMETERS LESS THAN 15 μm IN LIQUID CHROMATOGRAPHY

M. KREJČÍ*, K. TESAŘÍK, M. RUSEK and J. PAJUREK
*Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, Brno 61142 (Czechoslovakia)*

## SUMMARY

The flow characteristics of capillary columns at flow-rates up to $10^{-5}$ μl/sec have been studied experimentally as a function of the column diameter and of the pressure drop. Theoretical conclusions based on the Poiseuille equation and band broadening for unsorbed solutes have been tested.

The preparation of glass capillary columns is described, and the rôle of the glass melting temperature is discussed. The inner diameters (5–34 μm) of the columns were measured both by microscopy and hydrodynamically. The maximum difference between the two measurements was 2.8 μm, but in most cases it did not exceed 1.5 μm. The modified flame-ionization detector was used.

## INTRODUCTION

The development of liquid chromatography in capillary columns has led to the use of columns with very small diameters on the grounds of efficiency and the time required for analysis[1–4]. However, scepticism as to whether such usage can be justified has arisen because of the untried technology for the preparation of capillary columns with diameters, $d_c < 15$ μm, and the lack of suitable sampling and detection methods. The present paper describes an attempt to solve some of these problems.

We have examined experimentally some of the significant parameters in capillary liquid chromatography, such as the dependences of the dead time, number of theoretical plates and the pressure drop on the diameter of the column. In addition, hydrodynamic values are used to compare the diameters of capillary columns with diameters at discrete points determined with the aid of a microscope in order to evaluate the homogeneity of the capillary column throughout its length.

Previous studies[5–17] have made use of open tubular capillary columns, usually with diameters from 50 to 30 μm. The liquid–liquid system has most often been used, although adsorption and even ion-exchange liquid chromatography have been employed[18]. Attention was therefore concentrated upon columns with diameters less than 30 μm and on the liquid–liquid system.

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## THEORETICAL

In order to study the influence of the diameter of the capillary column on some chromatographic parameters, we started from a relationship derived from the Poiseuille equation

$$t_m = \varphi \eta L^2/d_c^2 \Delta p \tag{1}$$

where $\varphi$ is the column resistance parameter (= 32 for capillary columns), $\eta$ is the viscosity of the mobile phase, $L$ is the column length, $d_c$ is the column diameter, $\Delta p$ is the pressure drop in the column and $t_m$ is the dead retention time.

The dead retention time and thus also the analysis time increase for a given capacity ratio, $k$, with decreasing column diameter, provided the other parameters in eqn. 1 remain constant. However, if the optimum velocity of the mobile phase, $u_{opt}$, is employed, which corresponds to the minimum height equivalent to a theoretical plate for an unsorbed solute, $H_{min}$

$$H_{min} = 2\sqrt{BC_m} \qquad u_{opt} = \sqrt{B/C_m} \tag{2}$$

where the coefficient of longitudinal diffusion $B = 2 D_m$ and the coefficient of the mass transfer in the mobile phase

$$C_m = \frac{1 + 6k + 11k^2}{1 + k^2} \cdot \frac{d_c^2}{96 D_m}$$

the corresponding retention time for an unsorbed solute can be expressed as

$$t_m^* = L d_c/13.9 D_m \tag{3}$$

where $D_m$ is the diffusion coefficient of the solute in the mobile phase. Under these conditions ($u_{opt}$ and constant $L$ and $D_m$), the dead retention time decreases with decreasing diameter of the capillary column. For high column efficiency, it is necessary that extra column contributions to the height equivalent to a theoretical plate are negligible.

For the total time constant of the detector, $t_d$, the following conditions must be satisfied

$$t_d \leqslant t_m/2\sqrt{N} \tag{4a}$$

$$t_d \leqslant (Lh)^{1/2} d_c^{3/2}/2 D_m v \tag{4b}$$

where $N$ is the number of theoretical plates, $h$ is the reduced height equivalent to a theoretical plate (= $H/d_c$) and $v$ is the reduced velocity of the mobile phase (= $u d_c/D_m$). At the optimum velocity of the mobile phase, relationship 4a can be expressed as:

$$t_d^* \leqslant \frac{t_m^*}{2}\sqrt{\frac{0.29 d_c}{L}} = \frac{1}{51.6} \cdot \frac{\sqrt{L}\, d_c^{3/2}}{D_m} \tag{5}$$

Requirement of the time constant of the detector diminishes, *i.e.*, even a higher value of the detector time constant can be admitted (according to eqn. 4 or 5) under the assumption that $N$ decreases or $d_c$ increases. For instance, when $L = 1$ m, $D_m = 1 \cdot 10^{-9}$ m$^2$/sec and $d_c = 5$ μm, $t_d = 0.22$ sec, while when $d_c = 10$ μm, $t_d = 0.62$ sec. By substituting real values into relationship 4 or 5, the values of $t_d$ obtained are so small that the technical requirements of the design of the classical detection methods such as spectrophotometry, fluorometry, refractometry, etc., are immediately obvious. All these methods, based on the measurement of a change in an analytical property, require that the cuvettes employed have lengths of 0.01–0.1 mm and diameters equal to the column diameter. These requirements are unrealizable. Still less realizable therefore are any connections between the column and the detector.

For the reasons mentioned above, we consider transport detectors as promising. In such detectors the solute is transported quickly from the column outlet into the detection system where it gains a velocity substantially higher than the velocity of the mobile phase in the column. Examples are mass spectrometric detectors, flame ionization detectors[19] and their modifications and electrochemical detectors.

## EXPERIMENTAL AND RESULTS

### *Drawing of capillaries*

Glass can be applied to advantage in the preparation of capillaries of this type, owing to the properties described previously[12,20]. Capillaries are drawn in the device described by Desty *et al.*[21]. The diameters required can be drawn in a single or double run. The former procedure is commonly used for capillaries with larger inner diameters. It is necessary that the initial glass tube has dimensions about 8 × 0.3 mm in order for a suitable outer diameter (0.7–0.8 mm) to be obtained with an orifice of 30 μm or less. The latter procedure makes it possible to prepare a suitable capillary without the use of a thick glass tube[22]. A capillary of 0.95 mm O.D. is first drawn from a commonly available 7 × 1 mm tube and is then inserted into another 7 × 1 mm tube. Both tubes are then drawn into a capillary of 0.7–0.8 mm O.D. The inner diameter of this composite capillary corresponds to the dimension that is required.

The temperature of the oven in the drawing device is decisive for either procedure. The start of drawing is dependent on the melting temperature of the glass and, dynamic equilibrium in the oven having been reached, the dimensions of the capillary are controlled by the following relationship

$$d_{c1}/d_{c2} = \sqrt{c_1}/\sqrt{c_2}$$

where $d_{c1}$ and $d_{c2}$ are the diameters of the tube and the capillary, respectively, and $c_1$ and $c_2$ the velocities of the tube feeding and the capillary drawing from the oven, respectively. If the temperature increases and the glass is overheated, the capillary closes inside and the inner diameter is thus diminished. An increase of about 30°K (above the drawing temperature at which the relationship $d_{c_1}/d_{c_2} = \sqrt{c_1/c_2}$ is valid) will result in a solid glass rod. The effect of temperature on capillary narrowing is shown in Tables I and II and Fig. 1.

The temperature range in which capillaries having the required diameters can be drawn is 20–30°K (Fig. 2) and is, of course, different for each kind of glass.

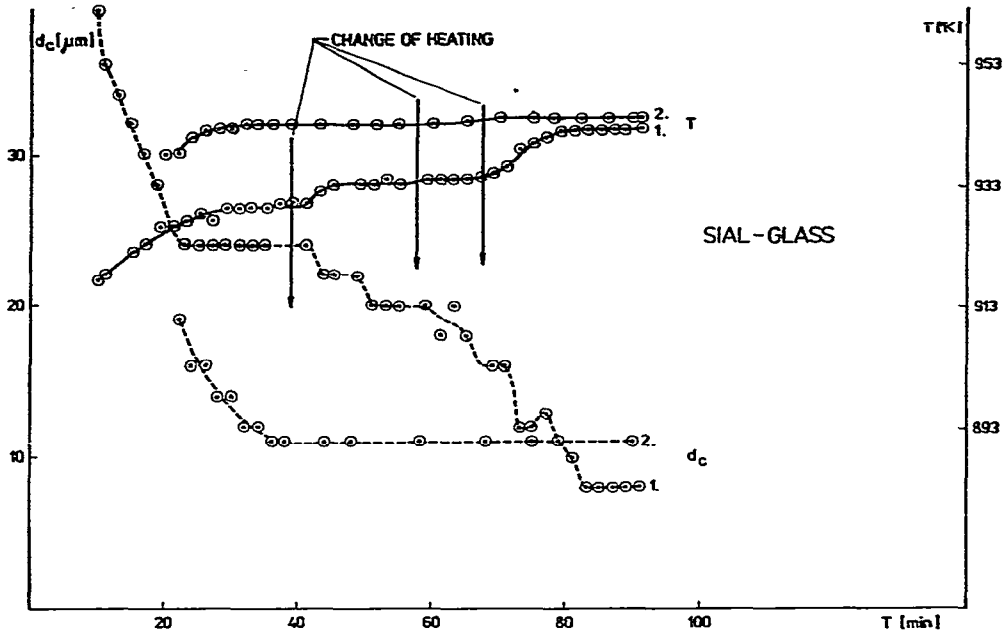



Fig. 1. Dependence of temperature and column diameter on time. 1, Changes of $d_c$ as a function of temperature changes $i$; 2, constancy of $d_c$ at constant oven temperature.

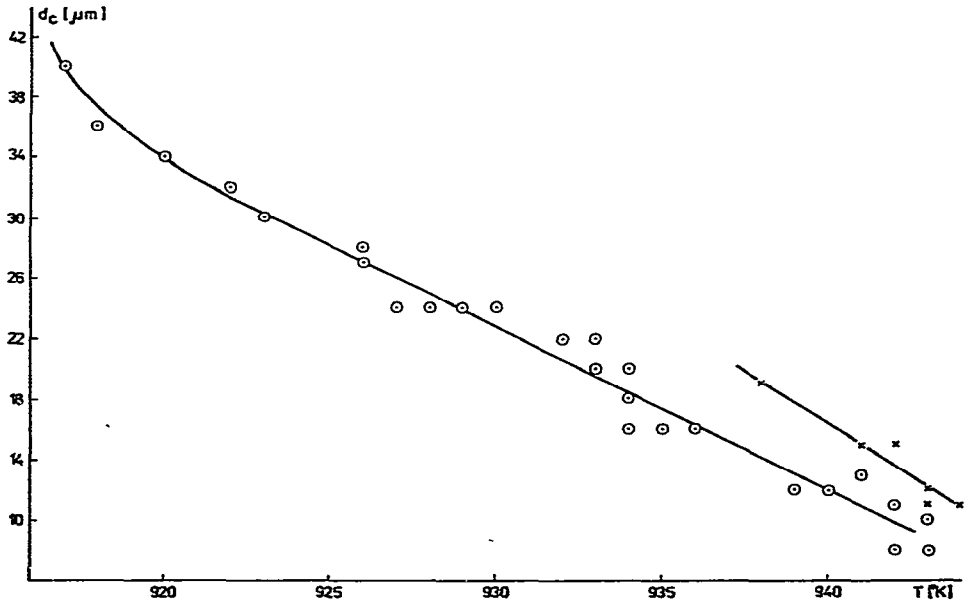



Fig. 2. Dependence of column diameter on temperature. Capillary A (⊙); capillary B (×).

TABLE I

DEPENDENCE OF THE CAPILLARY DIAMETER ON THE TEMPERATURE OF THE OVEN IN THE DRAWING DEVICE

| *Time (min)* | *Temperature (°K)* | $d_c$ *(μm)* | *Time (min)* | *Temperature (°K)* | $d_c$ *(μm)* |
|---|---|---|---|---|---|
| 10 | 917 | 40 | 51 | 933 | 20 |
| 11 | 918 | 36 | 53 | 934 | 20 |
| 13 | 920 | 34 | 55 | 933 | 20 |
| 15 | 922 | 32 | 59 | 934 | 20 |
| 17 | 923 | 30 | 61 | 934 | 18 |
| 19 | 926 | 28 | 63 | 934 | 20 |
| 21 | 926 | 25 | 65 | 934 | 18 |
| 23 | 927 | 24 | 67 | 934 | 16 |
| 25 | 928 | 24 | 69 | 935 | 16 |
| 27 | 927 | 24 | 71 | 936 | 16 |
| 29 | 929 | 24 | 73 | 939 | 12 |
| 31 | 929 | 24 | 75 | 940 | 12 |
| 33 | 929 | 24 | 77 | 941 | 13 |
| 35 | 929 | 24 | 79 | 942 | 11 |
| 37 | 930 | 24 | 81 | 943 | 10 |
| 39 | 930 | 24 | 83 | 942 | 8 |
| 41 | 930 | 24 | 85 | 943 | 8 |
| 43 | 932 | 22 | 87 | 943 | 8 |
| 45 | 933 | 22 | 89 | 943 | 8 |
| 49 | 933 | 22 | | | |

*Modification of the internal surface*

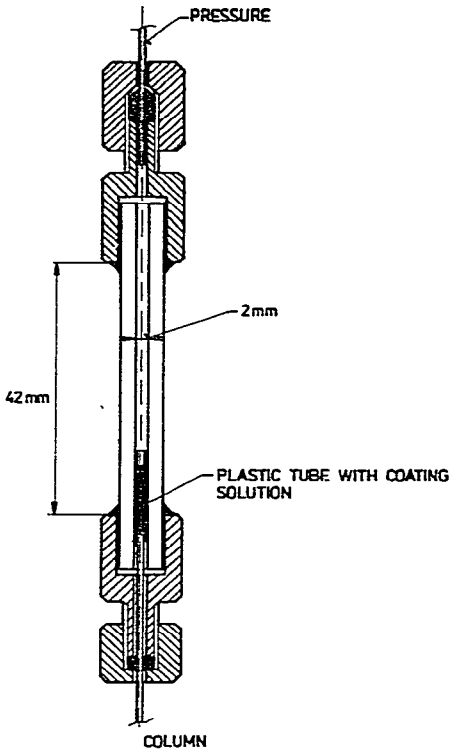
Etching of the internal surface of a glass capillary can be performed in the gaseous phase with hydrogen chloride, hydrogen fluoride, methyl trifluorochloroethyl ether, etc., or in the liquid phase with acidic or basic reagents. The procedures for the gaseous phase are less exacting since relatively low pressures, about 1–2 MPa, of an inert gas are sufficient for filling the capillary and activating its surface. In order to fill the capillaries with liquids, the operating pressures must be increased to 10–15 MPa and the probability of capillary blocking during filling or washing is greater.

The device for capillary filling with gases, vapours or liquids should have a

TABLE II

DEPENDENCE OF CAPILLARY DIAMETER ON THE OVEN TEMPERATURE AT CONSTANT OPERATING CONDITIONS

| *Time (min)* | *Temperature (°K)* | $d_c$ *(μm)* | *Time (min)* | *Temperature (°K)* | $d_c$ *(μm)* |
|---|---|---|---|---|---|
| 22 | 938 | 19 | 34 | 943 | 12 |
| 24 | 941 | 16 | 36 | 943 | 11 |
| 26 | 942 | 16 | 38 | 943 | 11 |
| 28 | 942 | 14 | 48 | 943 | 11 |
| 30 | 942 | 14 | 75 | 944 | 11 |
| 32 | 943 | 12 | 90 | 944 | 11 |



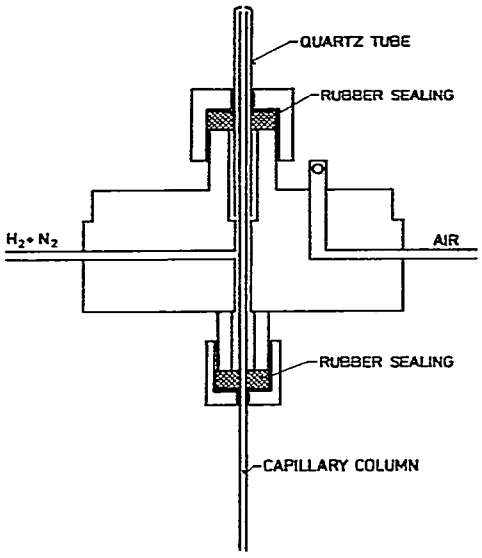




Fig. 3. Device for coating capillaries under pressure.
Fig. 4. Diagram of the burner of the flame ionization detector.

small working volume with respect to the small volume of the capillaries (up to 10 $\mu$l) and should be able to withstand even higher operating pressures. To fill the capillary with a liquid, a short polyethylene capillary (Fig. 3), containing a measured volume of the liquid is placed at the inlet of the glass capillary in a glass pressure tank. The pressure is increased and the liquid is forced into the capillary. The velocity of the liquid forced into the capillary is observed from the decrease in level in the polyethylene capillary. This capillary serves as a pressureless transparent reservoir of the liquid. The passage of the liquid is observed at the outlet of the glass capillary to which another thin polyethylene capillary is connected. The liquid can thus be collected in the latter capillary and forced out with gas pressure.

The concentration of the solution, velocity of filling and operating pressure are determined by the inner diameter of the capillary. The internal surface of the capillary diminishes linearly with decreasing diameter, while the volume of the liquid or the vapour in the capillary decreases with the square of the diameter. This decrease may be compensated by increasing the concentration or repeating the process until a regular stationary phase film or adsorption layer on the capillary wall is obtained.

*Detection technique*

A special burner was designed for liquid chromatography capillary columns, which was used in flame ionization and in alkali flame ionization detectors. The

burner (Fig. 4) consists of a quartz tube into which one tip of the capillary column is inserted. The column outlet is thus washed with a hydrogen–nitrogen mixture (50:50 v/v). The temperature of the end of the column can be varied from room temperature up to *ca.* 1000°K, depending on the type of burner and the distance from the flame. Under suitable conditions, the velocity of transfer into the detector is identical for solutes with boiling points within the range 350–600°K.

The flame ionization detector was of a common design with electrometric amplifiers, Vibron Model 33C (Electronic Instruments, Richmond, Great Britain) and one manufactured by Laboratory Instruments (Prague, Czechoslovakia). The alkali flame ionization detector in dual arrangement[23,24] was operated with the same electrometric amplifiers.

The flame ionization detector can also be used with such mobile phases for which the detector provides a response. If the detector response to solute *i*, $R_i^{H_2O}$, with water as the mobile phase is employed as a standard, then the detector response, $R_i$, to a mobile phase containing one detectable component b (*e.g.*, methanol) is determined by

$$R_i = R_i^{H_2O}\left(1 - \sum C_b^{eff} y_b \Big/ \sum C_i^{eff}\right) \quad (6)$$

where $C^{eff}$ is the effective number of carbon atoms of component b or solute *i* and $y_b$ is the molar fraction of component b in water. The detector response thus decreases as the value of the fraction at the right-hand side of eqn. 6 increases; likewise, in gas chromatography it decreases with the increasing tension of the stationary phase leaving the column for the detector[25]. A negative response is obtained in the case when $\sum C_i^{eff} < \sum C_b^{eff} y_b$. The ionization efficiency of the flame ionization detector used was 0.02 C/mole for isopropanol in water +5% methanol as mobile phase. The detector efficiencies for other solutes were similar.

The alkali flame ionization detector extends substantially the application range[26] of this detection principle in capillary liquid chromatography. For instance, a hydrocarbon mobile phase can be employed for halogen and phosphorus containing compounds. Sufficient sensitivity of detection of these substances is ensured by the high selectivity of the detector response.

A spectrophotometric detection using a scavenger liquid[12] was also used to measure retention time. A Variscan flow-through cuvette (volume 8 μl; Varian, Palo Alto, CA, U.S.A.) was washed with a mobile liquid with a ratio of mobile phase flow-rate from the capillary column to scavenger liquid flow-rate of 1:500–10,000 in such a way that the chromatogram obtained from measurements in the capillary column was not affected by the cell volume.

*Hydraulic measurements of the column diameter*

The homogeneity of the diameter of the capillary column throughout its length was checked for several columns by breaking the column and measuring with the aid of a microscope. The common procedure of determining the diameter at the beginning and at the end of the column was not considered sufficient when investigating a new method of preparation of glass columns.

Eqn. 1 was used to calculate the diameter of the capillary column. The dead retention time, $t_m$ (sec), the length of the capillary column, $L$ (m), and the pressure at

TABLE III

DIAMETERS OF CAPILLARY COLUMNS MEASURED BY MICROSCOPY AND CALCULATED ACCORDING TO EQN. 1

| *Column No.* | $d_c$ *(μm)* | | $\pm\sigma$ *(μm²)* | $\pm\sigma_{rel}$ *(%)* | *L (m)* | *Mobile phase* |
|---|---|---|---|---|---|---|
| | *Microscope* | *Calculated* | | | | |
| 1 | 5 | 4.8 | 0.13 | 2.70 | 1.00 | Water + 2% methanol |
| 2 | 8–9 | 8.0 | 0.17 | 2.12 | 2.20 | Isopropanol |
| 3 | 8–9 | 7.3 | 0.38 | 5.20 | 2.20 | Water + 5% methanol |
| 4 | 8–9 | 7.7 | 0.23 | 2.98 | 2.20 | Water + 5% methanol |
| 5 | 8–9 | 8.6 | 0.31 | 3.63 | 1.65 | Cyclohexane |
| 6 | 8 | 8.5 | 0.12 | 1.47 | 2.70 | Cyclohexane |
| 7 | 13 | 11.4 | 0.49 | 4.36 | 1.40 | Methanol |
| 8 | 13 | 13.7 | 0.68 | 5.97 | 1.60 | Methanol |
| 9 | 13 | 11.3 | 0.32 | 2.83 | 2.06 | Cyclohexane |
| 9a | 6–8 | 13.7 | 0.37 | 2.71 | 2.05 | Cyclohexane |
| 10 | 15 | 16.3 | 0.34 | 2.08 | 3.60 | Water |
| 11 | 17 | 16.9 | 1.24 | 7.30 | 2.05 | Cyclohexane |
| 12 | 17 | 17.1 | 1.73 | 10.10 | 1.96 | Cyclohexane |
| 13 | 34 | 37.6 | 11.77 | 31.31 | 2.00 | Cyclohexane |

the column inlet, $\Delta P$ (MPa), were measured experimentally. The following values were assumed: $\varphi = 32$; viscosities (N · sec/m²) at 295.7°K, $\eta_{H_2O} = 0.0942$, $\eta_{MeOH} = 0.0548$, $\eta_{C_6H_{14}} = 0.0306$, $\eta_{i\text{-PrOH}} = 0.195$ and $\eta_{cyclohexane} = 0.0710$. Table III shows the satisfactory agreement between the diameter at the beginning of the column determined by microscopy and the diameter calculated by using eqn. 1. Each $d_c$ value was calculated as the average of measurements performed at up to ten different mobile phase flow-rates (at ten different pressures at the column inlet). The standard deviation of an individual measurement was on the average 3.6%. These measurements were also performed at various points of the same column and for selected columns with different mobile phases. The values of the standard deviation were in the range 6–8%.

In some instances, particularly for capillary columns with diameters $d_c < 15$ μm, anomalies in the mobile phase flow-rate were observed in the course of measure-

TABLE IV

CHANGE IN $d_c$ DETERMINED ACCORDING TO EQN. 1 IN THE COURSE OF THE MEASUREMENT

$L = 2.5$ m.

| $d_c$ *(μm)* | | $\pm\sigma$ | $\pm\sigma_{rel}$ *(%)* |
|---|---|---|---|
| *microscope* | *calculated* | *(μm)* | |
| 6–7 | 5.7 | 0.194 | 3.4 |
| 6–7 | 6.3 | 0.154 | 2.5 |
| 6–7 | 6.9 | 0.111 | 1.6 |

ment. The rapid response of the flame ionization detector made it possible to measure not only the overall change in the flow-rate, appearing as a change in $t_m$, at a constant pressure, but also an instantaneous change in the flow-rate, appearing as a periodic decrease almost to zero followed by its re-establishment. In some instances, the mobile phase flow-rate ceased, as described earlier[12]; in the majority of instances, however, a pressure of up to 16 MPa was not sufficient to renew the flow-rate.

Table IV shows an example of the change in flow-rate and thus also the change in the value of $d_c$ calculated for a column with a diameter of $d_c$ = 6–7 μm (microscopy). The height equivalent to a theoretical plate was measured simultaneously with the parameters required for the calculation of $d_c$. The dependence of the reduced values is shown in Fig. 5. Boundary values, marked on this graph as 5 and 9 μm, were measured independently in other columns. The column described in Table IV and Fig. 5 became blocked after the injection of about 80 samples of isopropanol. At first, the flow-rate could be re-established temporarily by an increased pressure; ultimately, at a pressure of 30 MPa and at 80°C, the column remained blocked. Blocking of the inlet or outlet of the column was circumvented by gradual removal of sections at the column ends. It is assumed that the observed phenomenon is associated with the presence of surface active substances in the binary mobile phase.

*Measurement of the efficiency of capillary columns*

The dependence of the reduced height equivalent to a theoretical plate, $h$, on the reduced velocity, $v$, for an unsorbed solute (isopropanol) in columns with diameters $d_c$ = 15, 14, 9 and 5 μm is presented in Fig. 6. Columns of diameter $d_c$ = 9 μm or larger exhibit dependences which deviate significantly from the theoretical dependence, the values of $h$ being about four-fold greater than expected. However, the theoretical values are approached at the curve minimum and at low reduced velocities. The column of diameter 5 μm exhibits even great deviations although it was studied under identical conditions. In this case, the values of the reduced plate height approach the theoretical ones at low reduced velocities, but in the region of the minimum and at higher linear velocities the difference between the experimental and theoretical values of $h$ increases rapidly. The main reason for this phenomenon would

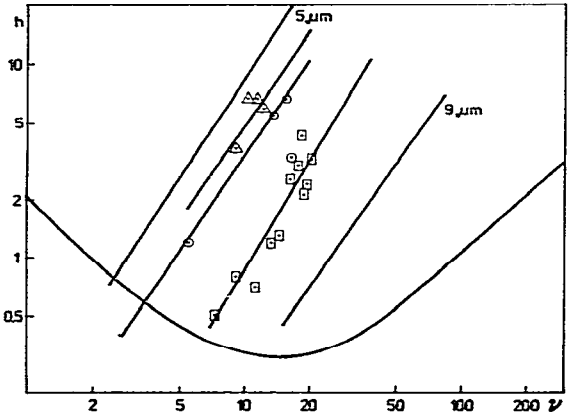



Fig. 5. Dependence of the reduced height equivalent to a theoretical plate, $h$, on the reduced velocity, $v$, for a column with $d_c$ = 6–7 μm. Apparent diameter: ≈5.7 μm (△); ≈6.3 μm (○); ≈6.9 μm (□).

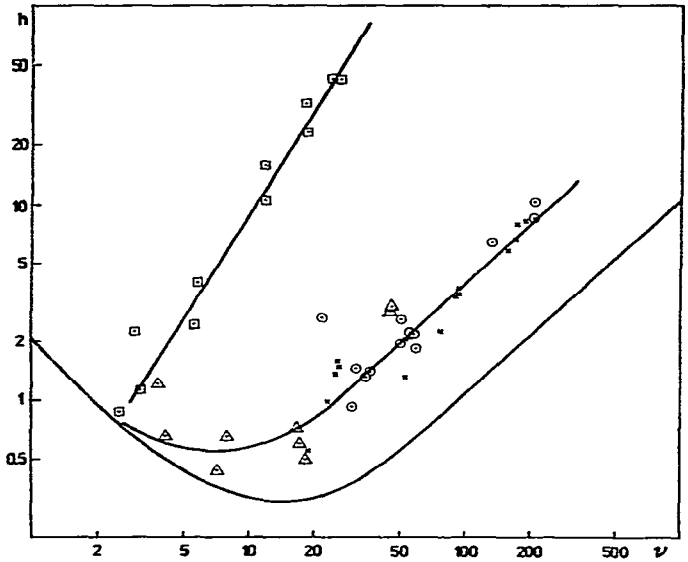



Fig. 6. Dependence of $h$ on $v$ for the columns with $d_c$ = 15 μm (○), 14 μm (×), 9 μm (△) and 5 μm (□).

seem to be that the demands placed on the detection mode are so great that they are not satisfied by the given arrangement.

The dependence of the detection time, $t_d$, calculated according to eqn. 4b, on the difference between the theoretical and experimental reduced plate heights is presented in Fig. 7. This shows that a column with $d_c$ = 5 μm requires $t_d$ to be of the order of seconds, which could not be achieved with our flame ionization detector, not only with respect to the electronics but also probably because of the speed of the solute transfer into the detection system. However, the detector is suitable for columns with larger diameters, where the required value of $t_d$ is larger.

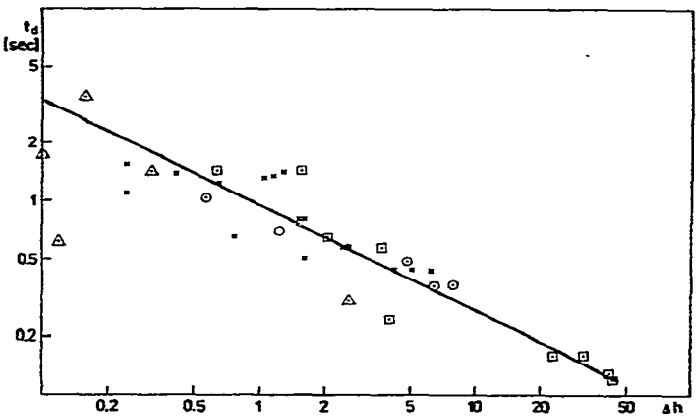



Fig. 7. Dependence of detection time, $t_d$ (according to eqn. 4), on the difference between the theoretical and experimental values of the reduced height equivalent to a theoretical plate, $\Delta h$. Other conditions as in Fig. 6.

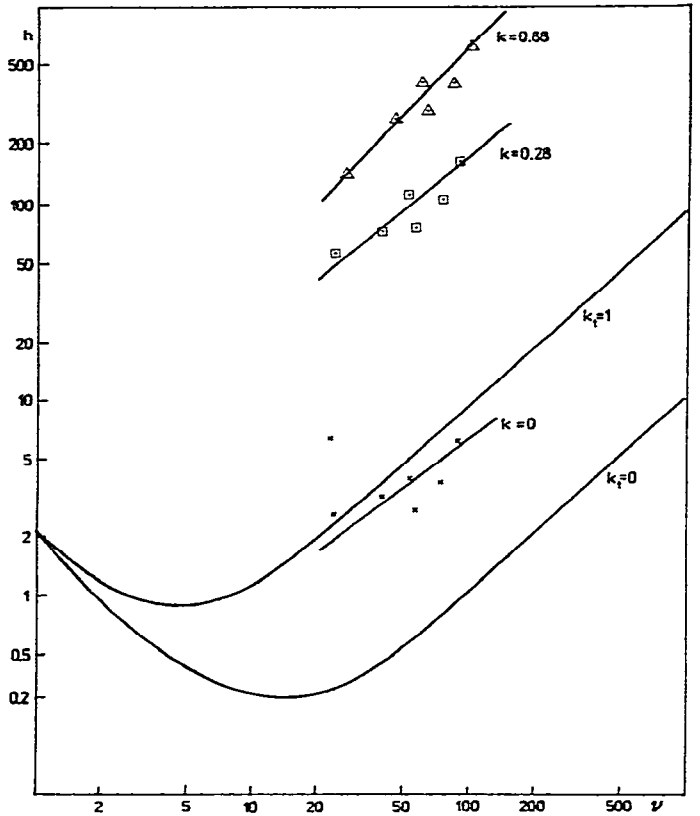



Fig. 8. Dependence of $h$ *vs.* $v$ for *o*-nitrobenzaldehyde ($k = 0$), *m*-cresol ($k = 0.28$) and β-naphthol ($k = 0.88$). Column: 3 m × 25 μm I.D., coated with 1,2,3-tris(cyanoethoxy)propane. Mobile phase: cyclohexanone saturated with 1,2,3-tris(cyanoethoxy)propane. UV detection at 220 nm. Theoretical values of $k_t$ were calculated for thickness of the stationary phase, $d_f = 1$ μm, $D_m = 1.2 \cdot 10^{-9}$ m²/sec and diffusion coefficient of the solute into the stationary phase, $D_s = 1.4 \cdot 10^{11}$ m²/sec.

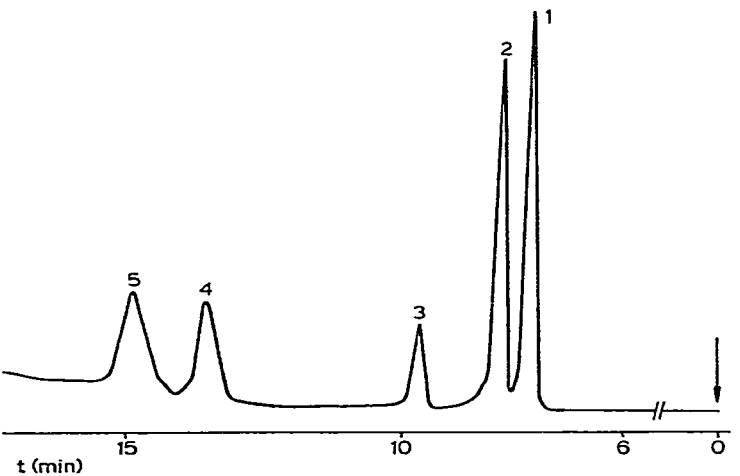



Fig. 9. Example of a chromatogram with flame ionization detection. Column: 3 m × 14 μm I.D. Stationary liquid: OV-101. Mobile phase: water. Solutes: 1 = triethylene glycol; 2 = *m*-cresol; 3 = 2,4-dimethylphenol; 4 = 2-methyl-4-ethylphenol; 5 = 2-isopropylphenol.

To evaluate the effect of retention on column efficiency, a glass capillary with $d_c$ = 25 μm was coated with 1,2,3-tris(cyanoethoxy)propane (Lachema, Brno, Czechoslovakia). The coating procedure and the detection were described earlier[12]. The results are shown in Fig. 8. The column efficiency is significantly lower and expected, and is ascribed to non-homogeneities in the film thickness; for the solutes used, non-ideal behaviour in both the mobile and stationary phases cannot be excluded.

## CONCLUSIONS

The possibility of preparing columns of 5 μm diameter or larger has been demonstrated. Column diameters determined with the aid of a microscope and by flow-rate measurements were in good agreement. Anomalies in the flow-rate were found for columns with small diameters, caused probably by surface active substances present in the capillary. Conditions for application of a flame ionization detector have been suggested. A typical separation is shown in Fig. 9.

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