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LIQUID CHROMATOGRAPHY IN OPEN-TUBULAR COLUMNS

THEORY OF COLUMN OPTIMIZATION WITH LIMITED PRESSURE AND ANALYSIS TIME, AND FABRICATION OF CHEMICALLY BONDED REVERSED-PHASE COLUMNS ON ETCHED BOROSILICATE GLASS CAPILLARIES

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SUMMARY

A theory is developed which shows that open-tubular columns will have well defined optimum diameters and lengths if limits are placed on the available pressure and analysis time. The optimum diameters are shown to be rather insensitive to choice of operating pressure and analysis time, and lie between 1 and 3 μm for a wide range of conditions.

A method of etching borosilicate glass capillaries to increase surface roughness and column capacity factors is described. Octadecylsilane is chemically bonded to these roughened surfaces and columns are operated in a reversed-phase mode. Detection of solutes is with an on-column fluorescence detector.

INTRODUCTION

Open-tubular columns offer the best means of achieving high separation efficiencies in gas chromatography. Recently the subject of open-tubular columns in liquid chromatography has received considerable attention. Theoretical aspects of open-tubular columns in liquid chromatography were discussed in the papers by Knox and Gilbert[1], Knox[2] and Guiochon[3]. In this paper a simple theory which predicts optimal physical dimensions for open-tubular columns in liquid chromatography given limitations on available pressure and analysis time is described. A growing body of experimental work with open-tubular liquid chromatography columns now exists[4–20]. The majority of this work involves etched soda-lime glass capillaries used in either an adsorption mode or with liquid stationary phases in a partition mode. This paper describes columns fabricated from borosilicate glass using a novel etching technique followed by chemical bonding of an octadecylsilane stationary phase. A simple and effective sample "injection" system applicable in principle to any size capillary is also described. Detection appears to be the greatest obstacle to realization of working capillary systems, and suggestions for future research in this area are made.

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THEORY OF COLUMN OPTIMIZATION

We wish to use Golay's plate height equation[21] for open-tubular columns to decide how to best design a column to achieve the maximum number of theoretical plates. It is easy to show that if no restrictions are placed on the analysis time or pressure available there is no theoretical limit to the number of plates which may be generated[1]. We would rather limit these two variables, time and pressure, to realistic values and see what size of open-tubular column we should try to fabricate. Presumably high plate numbers are needed for analysis of complex mixtures, where components span a wide range of capacity factors. Thus we will not treat the capacity factor as a variable around which to optimize but will try to optimize the system overall instead.

The mobile phase velocity, v, in a tubular column is given by

$$v = \frac{Pr^2}{8\eta L} \tag{1}$$

where P is the applied pressure, r the column radius, η the mobile phase viscosity, and L the column length. The retention time, t, of a solute in this column is

$$t = \frac{L}{v}(1 + k') \tag{2}$$

where k' is the solute's capacity factor. Substitution of eqn. 1 into eqn. 2 yields

$$t = \frac{8\eta L^2(1 + k')}{Pr^2} \tag{3}$$

and the retention time is a function of the physical parameters of diameter, length, pressure, viscosity and capacity factor. We would like to maintain analysis time within reasonable limits, or in other words, choose a maximum time in which a solute with the largest capacity factor will elute. We would also like to set an upper limit on the pressure. Since the viscosity is determined by choice of mobile phase, and is not a particularly useful variable, we are left with only two variables, namely column radius and length. But eqn. 3 shows us that these two, now, are not independent variables. Choosing one immediately fixes the other. We may rewrite eqn. 3 as

$$r = \left[\frac{8\eta(1 + k')}{Pt}\right]^{\frac{1}{2}} L \tag{4a}$$

$$L = \left[\frac{Pt}{8\eta(1 + k')}\right]^{\frac{1}{2}} r \tag{4b}$$

where P, t, k', and η are now effectively constants.

We now ask the question as to what is the best column radius and length to achieve the maximum number of theoretical plates given these time and pressure

constraints. At this point we refer to Golay's equation for plate height[21], H, in an open-tubular column

$$H = \frac{2D}{v} + \frac{(1 + 6k' + 11k'^2)r^2v}{24(1 + k')^2D} \tag{5}$$

where D is the solute's diffusion coefficient in the mobile phase. We have neglected the resistance to mass transfer in the stationary phase as this has been shown to be negligible in both theory and practice when thin films of stationary phase are used[2]. By substituting the expression for velocity (eqn. 1) into this equation we get

$$H = \frac{16D\eta L}{Pr^2} + \frac{(1 + 6k' + 11k'^2)Pr^4}{192\,(1 + k')^2D\eta L} \tag{6}$$

We may now describe the total number of theoretical plates, N, as

$$N = \frac{L}{H} = \frac{192(1 + k')^2D\eta PL^2r^2}{3072(1 + k')^2D^2\eta^2L^2 + (1 + 6k' + 11k'^2)P^2r^6} \tag{7}$$

Since length is now a function of radius, we may use eqn. 4b to substitute for length in eqn. 7

$$N = \frac{24(1 + k')DPtr^2}{384(1 + k')D^2\eta t + (1 + 6k' + 11k'^2)Pr^4} \tag{8}$$

This equation describes what N values of the last eluting component will be, as a function of column radius, given the constraints on retention time and pressure. The number of plates as a function of column diameter is plotted for several pressures at a single analysis time in Fig. 1, and for several analysis times at a single pressure in Fig. 2. These plots show rather sharp maxima. At radii smaller than the optimum, excessive longitudinal diffusion leads to reduced performance. At radii larger than optimal, excessive resistance to mass transfer leads to lower plate counts. Thus we see that there is an optimum column radius and length, given certain limits on available time and pressure. The commonly held belief that smaller-diameter columns will yield ever-improving performance is not true if pressure is limited. Perhaps more important is that somewhere between 1 and 2 μm is the optimum column diameter for columns over a wide range of operating pressures and analysis times. This region of optimum diameter is fairly well defined, and is fairly insensitive to choice in operating pressure and analysis time. We feel that this defines the ultimate dimensional goal of open-tubular liquid chromatography. We must achieve succes in the 1–2 μm diameter range or we will not begin to realize the potential benefits of high efficiency. The optimistic side of this conclusion is that if we succeed in fabricating and operating columns of these diameters, the basic technology will be effective even if we decide to make fairly large changes in operating pressure or analysis time. It is worth noting that the same kind of theoretical considerations should be applicable to packed-column liquid chromatography. Thus there is probably an optimum particle size, somewhere around 1 μm, with which to pack columns. This size will be optimal for a wide range of pressures

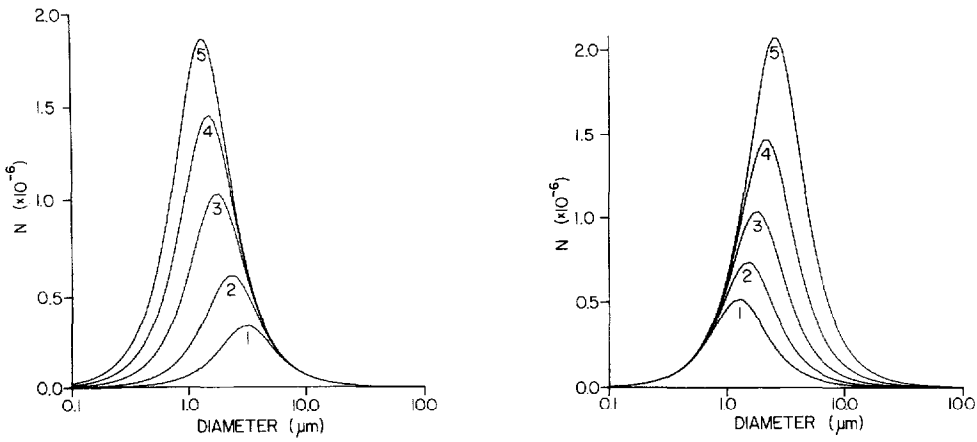

Fig. 1. Number of theoretical plates as a function of column diameter for five different pressures. $k' = 10$, $D = 1 \cdot 10^{-5}$ cm^2/sec, $\eta = 5 \cdot 10^{-3}$ P, $t = 2$ h. 1 = 300 p.s.i.g. (21 bar); 2 = 1000 p.s.i.g. (69 bar); 3 = 3000 p.s.i.g. (210 bar); 4 = 6000 p.s.i.g. (420 bar); 5 = 10,000 p.s.i.g. (690 bar).

Fig. 2. Number of theoretical plates as a function of column diameter for five different analysis times. $k' = 10$, $D = 1 \cdot 10^{-5}$ cm^2/sec, $\eta = 5 \cdot 10^{-3}$ P, $P = 3000$ p.s.i.g. (210 bar). 1 = 0.5 h; 2 = 1.0 h; 3 = 2.0 h; 4 = 4.0 h; 5 = 8.0 h.

and analysis times, and pursuit of significantly smaller diameter packings will probably be unnecessary.

The actual radius which is optimal for a given set of conditions may be found by differentiating eqn. 8 with respect to radius, setting the differential equal to zero, and solving for the radius. The resulting optimum radius is

$$r_{opt} = \left[\frac{384D^2\eta(1 + k')t}{(1 + 6k' + 11k'^2)P}\right]^{\frac{1}{4}} \tag{9}$$

Through use of eqn. 4b the corresponding optimum length for this optimum radius is

$$L_{opt} = \left[\frac{6D^2Pt^3}{(1 + k')(1 + 6k' + 11k'^2)\eta}\right]^{\frac{1}{4}} \tag{10}$$

Eqn. 9 clearly shows the insensitivity of the actual optimum radius on time and pressure. It is a 1/4 power function of time and an inverse 1/4 power function of pressure. Eqn. 10 shows that optimum length is an insensitive function of pressure. However, the optimum length, as a 3/4 power function of time, is almost linearly dependent on the available analysis time. It is almost correct to say that if more analysis time is available, more plates are best generated simply by using a longer column.

Finally, by substituting the optimum value for radius from eqn. 9 into eqn. 8 we get the maximum number of theoretical plates attainable with these pressure and time restrictions

$$N_{max} = \left[\frac{3P(1 + k')t}{8\eta(1 + 6k' + 11k'^2)}\right]^{\frac{1}{2}} \quad (11)$$

PRACTICAL CONSIDERATIONS

Column fabrication

A variety of column types have been used in open-tubular liquid chromatography. Adsorption and liquid–liquid partitioning systems have been most common, but ion-exchange[11], polystyrene-based reversed-phase[19], and chemically bonded reversed-phase[5,16,20] systems have also been used. It is likely that chemically bonded reversed-phase systems will prove to be the most useful mode in capillary liquid chromatography, based on experience with conventional packed columns. Although liquid stationary phases have been popular in open-tubular columns so far, we feel that due to the usual difficulties of stationary phase bleeding, especially when using mobile phase gradients, chemically bonded stationary phases will be preferred in the long run. Regardless of the mode of column operation a common problem in any open-tubular system is achieving useful capacity factors with mobile phases of realistic composition. This usually requires some method of increasing the surface area of the capillary. Several means are available, including bonding fine particles to the capillary surface[9] or etching the surface by chemical means[8,14] as is common in capillary gas chromatography. In our work we wished to detect fluorescent solutes while they were still in the capillary column by illuminating the capillary with ultraviolet (UV) light. The UV-transmitting characteristics of borosilicate glass are superior to soda-lime glass, and so we chose to work with borosilicate glass. Fused silica would be even better from an optical point of view, but less is known about surface etching and modification of fused silica[16]. It has long been known that a phase separation will occur in borosilicate glass if it is maintained at elevated temperatures. A water-insoluble phase composed primarily of silica and a water-soluble phase composed mainly of the remaining metal oxides are found. In the case of Pyrex type 7740 borosilicate glass the regions of water-soluble phase are not interconnected due to the high (80%) silica content[22,23]. Thus only the surface of the glass may be leached of its water soluble metal oxides, leaving a rough surface composed mainly of silica. This surface should be ideal for chemical bonding of a stationary phase.

Sample injections

The dimensions of optimized columns are quite small. Indeed, the total volume of a column with a 2-μm diameter and 2 m length is only 6 nl. This would seem to preclude use of any of the techniques of sample injection used with conventional packed columns. Sample loop injections or direct on-column syringe injections seem essentially impossible with micron-sized columns. Attaching short lengths of capillary filled with sample to the column inlet as described by Tsuda *et al.*[5] is also not feasible, as successful alignment of micron-sized holes without leaks or excessive dead volumes is extremely unlikely. It would appear that some form of splitting arrangement will be the best solution. This could be either a dynamic split where sample flow is divided between the column and waste[13,24] or a static split as will be described later in this paper.

Detection

Detection seems an even more difficult problem, as samples will generally be in the sub-picogram range. This will require use of the most sensitive mechanisms of detection available, and appears as the largest obstacle to actual realization of open-tubular columns as a useful technique. Potential detectors may be divided into two categories, on-column and post-column. Where feasible, on-column detection is probably to be preferred as it avoids extra-column band broadening invariably associated with post-column detection. On-column detection has been described for UV absorption in capillaries of rather large diameter[16,17]. As columns of smaller diameter are used, UV-absorption detection will probably prove untenable in an on-column mode as the optical path length will be too short. Post-column detection has also been described with open-tubular columns. Here large make-up flows must be added to the column effluent to minimize post-column band broadening. These make-up flows dilute the sample considerably, thus making detection more difficult[12]. Post-column detection will probably be of use only when it is based on a detection principle which cannot be performed on-column.

Of the possible modes of detection the following appear to us to show some hope of adequate sensitivity for use as detectors in capillary liquid chromatography. Fluorescence shows good promise and will be used for detection in this paper. Absorption detection via the laser-based thermal lens effect may have adequate sensitivity[25]. On-column refractive index detection, based on light scattering from the cylindrical glass–fluid interface in the capillary, may be possible and is being pursued in this laboratory. Amperometric electrochemical detection is quite sensitive, and has been used in conjunction with packed microcapillaries[26]. Photoionization detection by post-column vaporization of solvent and samples is also potentially sensitive. This requires the use of solvents which are not photoionized by the wavelength of light used, a requirement which proves to be fairly easy to meet[27]. We are pursuing this mode of detection not only because it may be a useful detector, but because it affords us a chance to learn something of the techniques of sample volatilization which may ultimately be useful in mass spectrometric detection. Mass spectrometers are especially attractive as a potential "detector" with capillaries. However, present day mass spectrometers have sufficient sensitivity only when operated in a selected-ion mode. Spectral scanning requires more sample than an optimal diameter capillary can provide. "Multichannel" detection such as is possible with a focal plane instrument described by Beynon *et al.*[28], or an ion-cyclotron resonance mass spectrometer[29] may eventually be sensitive enough to permit full spectra to be obtained on sub-picogram quantities. Sample vaporization prior to ionization in a mass spectrometer is a problem of special concern. Introducing sample as a jet of droplets as described by Tijssen *et al.*[12] is a possibility. Fortunately this is a time of active research in new methods of sample vaporization and ionization, and we may expect many new developments, such as fast-atom bombardment[30], in this area[31].

EXPERIMENTAL

Columns

Columns were drawn from Pyrex type 7740 borosilicate glass precision-bore capillary tubing obtained from Wilmad Glass Co. (Buena, NJ, U.S.A.) to an ap-

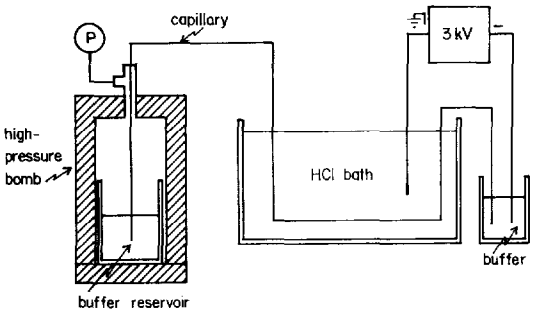

Fig. 3. Column electro-etching system.

proximate outside diameter of 0.6 mm on a Shimadzu (Kyoto, Japan) GDM-1B glass drawing machine. These capillaries were then heat-treated in a furnace for 24 h, after which they were placed in the etching apparatus shown in Fig. 3. In this system 0.2 *M* phosphate buffer at pH 7 was forced through the column via the home-made high-pressure bomb. The columns themselves were immersed in a vat of 3 *M* hydrochloric acid which was stirred and kept at a temperature of approximately 85°C. During etching a 3-kV d.c. potential was applied across the capillary wall by grounding the HCl bath and applying a negative potential to the buffer in the outlet reservoir. This electric field was found necessary to ensure that etching proceeded. Without the use of the field only about one out of three capillaries would etch successfully. With the field every attempt has yielded a successfully etched column. Following etching the columns were rinsed with distilled water and dried in a dry nitrogen flow at 140°C for at least 1 h. The capillaries were then filled with a 20% solution of dimethyloctadecylchlorosilane (Petrarch Systems, Levittown, PA, U.S.A.) in toluene, the ends sealed in a flame, and placed in an oven at 140°C for 1 h. The columns were then rinsed with toluene to remove reagents, and were extensively rinsed with mobile phase. At this point the columns were ready for use. Columns fabricated in this manner have proved very stable, with no loss in capacity factors or efficiency after extensive use or after storage for up to one year.

Injection of samples

Columns were connected with vespel ferrules to the "static" splitting injection system shown schematically in Fig. 4. Mobile phase was supplied from a simple gas-pressurized solvent reservoir. To inject a sample valve 2, a shut-off valve, was opened and valve 1, a four-port two-way valve, was positioned so that sample could be injected until it filled the splitting tee. Valve 2 was then closed and valve 1 returned so

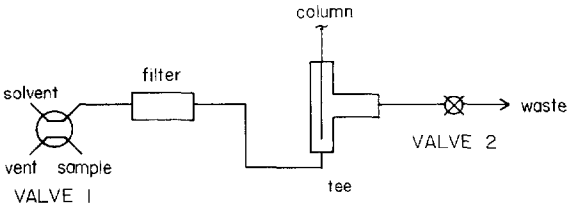

Fig. 4. Static splitting injection system.

that pressurized mobile phase was applied to the system, forcing some of the sample in the tee into the column. After a predetermined length of time valve 2 was opened so that the excess sample was rinsed from the tee. Finally, valve 2 was once again closed allowing chromatography to proceed. The volume of sample injected can be simply determined from the length of time sample is injected before valve 2 is opened to rinse remaining sample from the tee. A 2-μm filter is included in the system to prevent particles from plugging the column. This method of injection has proven convenient, effective, reproducible and reliable. Its one drawback is that it wastes most of the sample. This aspect will be difficult to engineer out of any injection system for extremely small capillaries. Valve 1 was obtained from Valco Instruments (Houston, TX, U.S.A.) and valve 2 and the filter were obtained from Scientific Systems (State College, PA, U.S.A.). The entire injection system was composed of stainless steel fittings.

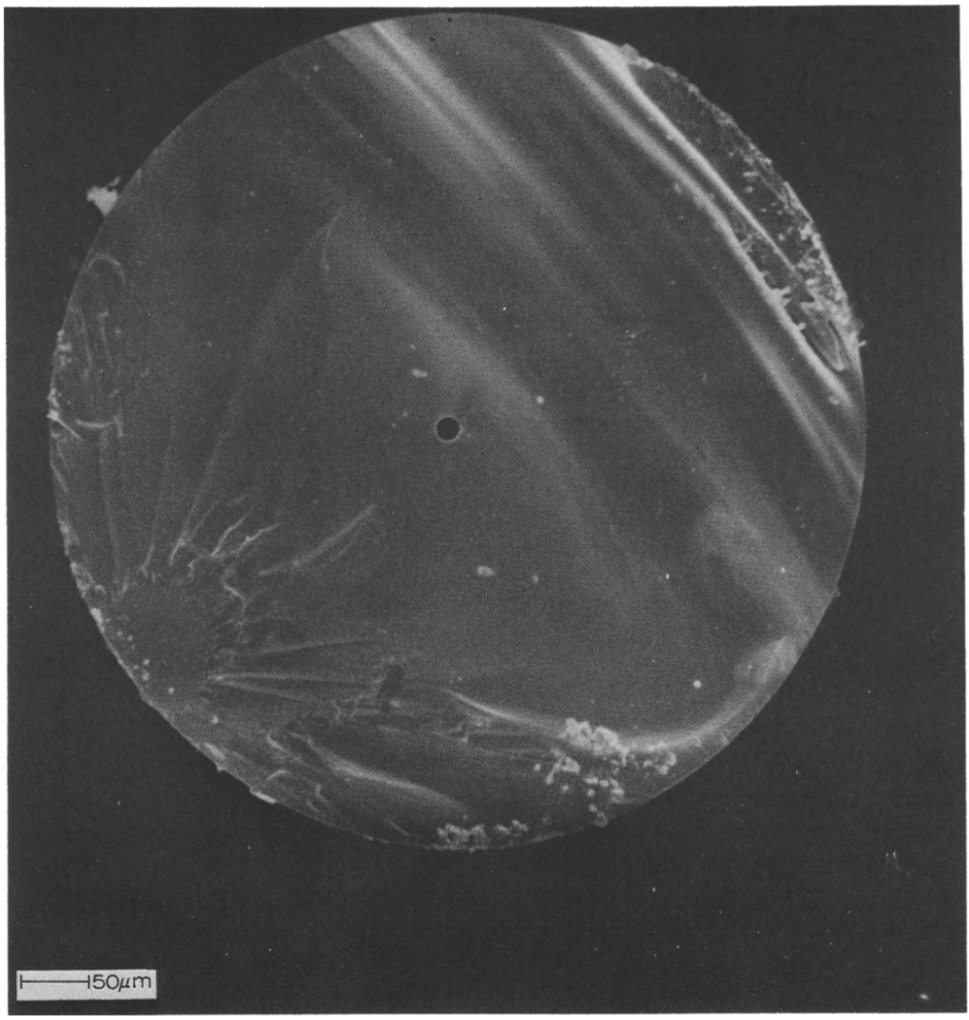

Fig. 5. Electron micrograph of end of a 15-μm I.D. glass capillary, column No. 10 from Table I.

Detection

In this work all detection was performed using a home-made on-column filter fluorometer. The light from a high-pressure mercury arc lamp is collimated, passed through a UV-transmitting filter, and focussed onto the capillary. Fluorescent emission is collected at a right angle to excitation with a lens, passed through a UV-blocking filter, and focussed onto a photomultiplier tube. Details of construction of this detector will be published separately.

RESULTS AND DISCUSSION

In order to gain an appreciation of the relative dimensions involved, Fig. 5 shows an end-on view of a 15-μm I.D. capillary taken with an electon microscope. The internal volume of the capillary is indeed small compared to the total volume of glass making up the capillary. As the I.D. of these capillaries is further reduced the O.D. will probably need to remain the same in order to retain mechanical strength and ease of connection of the capillary. The limited sensitivity of our present on-column fluorescence detector has restricted us to work with columns of 15 μm or more in diameter.

The first portion of Table I shows the results of heat treatment of 15-μm capillaries at several temperatures prior to etching. It is clear that treatment at 600°C for 24 h yields the largest capacity factors. In fact, the capacity factors increase 10-

TABLE I

EFFECT OF HEAT TREATMENT TEMPERATURE AND ETCHING TIME ON CAPACITY FACTORS

All columns 15 μm I.D. All columns were heat-treated for 24 h. Capacity factors for 9-methylanthracene were measured in a mobile phase of acetonitrile–water (35–65).

Column No.	*Heat treatment temperature (°C)*	*Etching time (h)*	*k'*
1	None	24	0.34
2	None	24	0.39
3	500	24	0.45
4	500	24	0.69
5	500	24	0.58
6	500	24	0.35
7	550	24	0.77
8	600	24	3.5
9	600	24	3.2
10	600	24	3.9
11	610	24	1.9
12	620	24	0.53
13	600	8	2.1
14	600	8	2.3
8	600	24	3.5
9	600	24	3.2
10	600	24	3.9
15	600	72	3.0

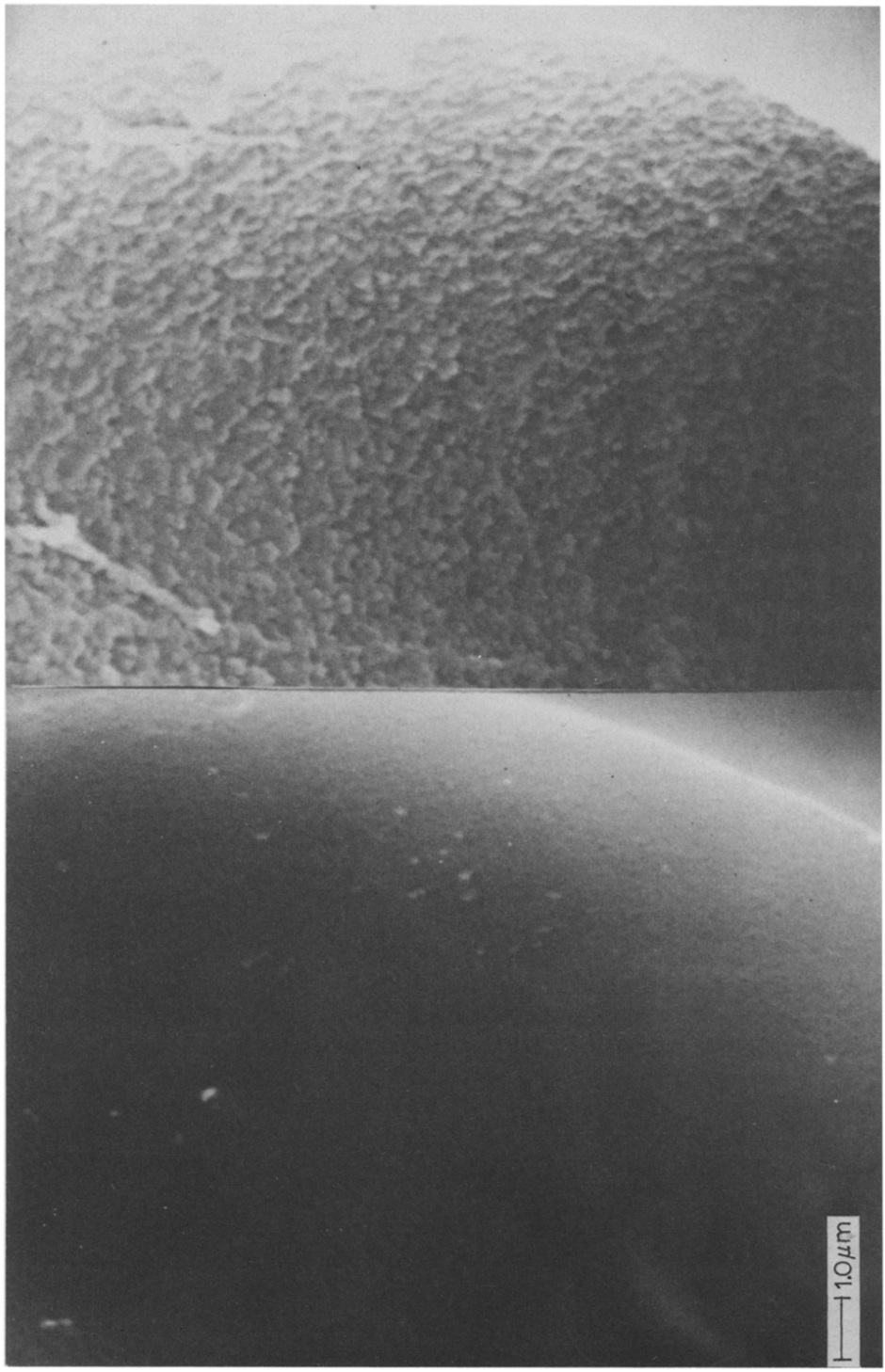

Fig. 6. Electron micrographs of inner surface of 15-μm capillaries. Left: column heat-treated for 24 h at 500°C, $k' = 0.45$ (column No. 3 from Table I). Right: column heat-treated for 24 h at 600°C, $k' = 3.9$ (column No. 10 from Table I).

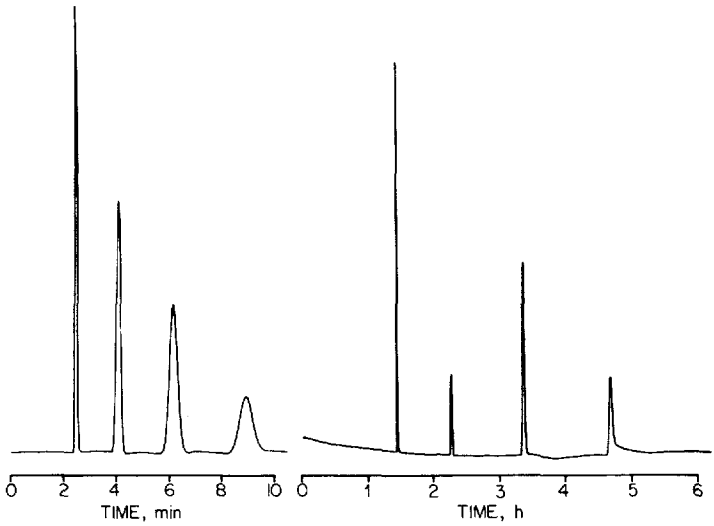

Fig. 7. Chromatograms of standards run in a 3 m × 32 μm I.D. column, mobile phase acetonitrile–water (50:50). Left: P = 100 p.s.i.g. (6.9 bar). Right: P = 5 p.s.i.g. (0.34 bar). Standards: 1 = riboflavin; 2 = 9-methylanthracene; 3 = perylene; 4 = benzo[*ghi*]perylene.

fold over a non-heat-treated smooth glass surface. We infer from this that treatment in this fashion produces a surface which is 10-fold rougher than a smooth glass wall. Heat treatment beyond 600°C leads to distinct decreases in capacity factor while at the same time the glass becomes quite brittle. Fig. 6 is a pair of electron micrographs of the inner walls of two capillaries treated in an identical manner, except that the left figure (smooth) was heat treated at 500°C while the right figure (rough) was treated at 600°C. The dramatic difference in roughness corresponds nicely to the dramatic difference in capacity factor. The roughened surface appears very uniformly "etched", with visible features having a size of a few tenths of a micron. End-on views of these

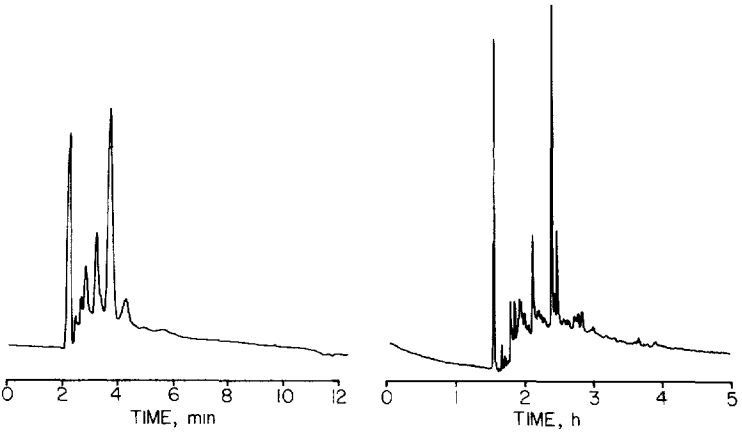

Fig. 8. Chromatograms of solvent-refined coal fluids in same column as Fig. 7. Conditions, left and right: as in Fig. 7. First peak: riboflavin dead-time marker. Sample: solvent-refined coal liquid extracted into acetonitrile–water (50:50).

etched capillaries show that the roughening is very superficial. This is desirable as it will not result in a thick layer of stagnant mobile phase and the associated band broadening. The second section of Table I shows the effect of etching time on capacity factor. It appears that etching is essentially complete somewhere between 8 and 24 h, and that more than 24 h of etching accomplishes no further increase in capacity factor. Indeed, after three days of etching the capacity factor is slightly lower than after one day, and the glass itself is extremely brittle and highly etched on its exterior as well as interior. Although we feel these results are promising we would like to see further increases in capacity factors, at least by another factor of four. Improved capacity factors will allow us to work in more realistic solvent systems containing less water. We expect to see capacity factors improve as column diameter is decreased as a general result of the trend of increasing surface-to-volume ratios in progressively smaller capillaries. Indeed, we have seen roughly a two-fold improvement in capacity factors when going from 65-μm to 15-μm diameter columns.

Fig. 7 shows two chromatograms of some polynuclear aromatic hydrocarbon standards run in a 32-μm diameter column. In the first case a faster mobile phase velocity is used, yielding 1800 theoretical plates for the third peak, which is perylene. In the second case a slower velocity is used yielding approximately 40,000 plates for perylene. This is an easily overlooked aspect of chromatography in long capillaries. The fast chromatogram, while reasonably efficient, was run at velocities far beyond the optimum velocity. In order to secure more plates, the mobile phase velocity is simply reduced by lowering the pressure, and quite high efficiencies are immediately available at the expense of longer analysis times. This particular use of capillaries can be quite convenient. This is well demonstrated in Fig. 8, where a sample obtained from a solvent-refined coal fluid is run at both high and low velocity. In the fast chromatogram, several peaks are seen, with little indication of the real complexity of the sample. Upon slowing down the mobile phase the true complexity of the sample begins to emerge, as each of the peaks in the fast chromatogram is seen to be composed of several peaks. Still higher separation efficiencies would undoubtedly reveal a much more complex mixture.

In two separate publications Tsuda and co-workers[5,20] have investigated chemically bonded octadecylsilane stationary phases. In the earlier work they bonded a trichlorooctadecylsilane to a "washed" borosilicate glass capillary of 60 μm I.D. In the later work they bonded a triethoxyoctadecylsilane to a base-etched soda-lime glass capillary of 23 μm I.D. In both cases the columns were operated at high enough mobile phase velocities such that the "C" term (resistance to mass transfer) of the Van Deemter equation should account for essentially the total measured height equivalent to a theoretical plate (HETP). In the 60-μm column using a mobile phase of acetonitrile–water (25:75) and biphenyl ($k' = 1.0$) as a solute, a value of 0.56 sec can be calculated for the "C" term. In the 23-μm column using a mobile phase of acetonitrile–water (50:50) and pyrene ($k' = 1.34$) as a solute, a value of 0.19 sec can be calculated for the "C" term. In both papers the authors commented that the separation efficiencies were less than expected, and were worse than results obtained using a liquid stationary phase in columns of the same diameter. They blamed resistance to mass transfer within the stationary phase as the likely cause. Since they used trifunctional silanes to obtain a polymeric stationary phase of increased capacity, a viscous stationary phase with increased resistance to mass transfer may have resulted.

In our work monolayers of stationary phase were obtained using mono-functional silanes. In our 32-μm column using perylene ($k' = 1.5$) as a solute, a value of 0.084 sec can be calculated for the "C" term (data from Fig. 7, left panel). This data from our 32-μm column may be compared closely with the data of Tsuda and co-workers on their 23-μm column, as identical mobile phases and similar sized solutes were used. Even though we used a larger-diameter column, we obtained a significantly smaller "C" term. This is interesting since resistance to mass transfer in the mobile phase should be proportional to the square of column diameter. From the point of view of column efficiency it appears that monolayers of stationary phase are superior to polymeric phases. In order to achieve useful capacity factors effective techniques of surface roughening are preferable to attempts to utilize polymeric phases.

In general, open-tubular capillaries have a number of advantages to offer, chief among these being high separation efficiencies. However, difficult problems must be overcome for the technique to be truly useful. Injections are not really difficult. The injector described in this paper is one of many designs which can work very effectively. Column fabrication is an important area for development. In general still smaller-diameter columns producing larger values of capacity factor and theoretical plates are needed. The prospects here are fairly good, and the next few years should see significant improvements in column fabrication. The most uncertain area is detection. Here we are farthest from our goal of realistic working systems, and any broadly significant developments are probably many years away. It is detection which will determine if liquid chromatography in capillaries is to be a real success.

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